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(54) Title: PROCESS FOR THE SYNTHESIS OF ETHERS OF AROMATIC ACIDS

(57) Abstract: Ethers of aromatic acids are produced from halogenated aromatic acids in a reaction mixture containing a copper (I) or copper (II) source and a diketone ligand that coordinates to copper.



WO 2008/079225 A1

TITLEPROCESS FOR THE SYNTHESIS OF
ETHERS OF AROMATIC ACIDS

5

This application claims the benefit of U.S. Provisional Application No. 60/876,570, filed 21 December 2006, which is incorporated in its entirety as
10 a part hereof for all purposes.

Technical Field

This invention relates to the manufacture of
15 ethers of hydroxy aromatic acids, which are valuable for a variety of purposes such as use as intermediates or as monomers to make polymers.

20 Background

Ethers of aromatic acids are useful as intermediates and additives in the manufacture of many valuable materials including pharmaceuticals and compounds active in crop protection, and are also
25 useful as monomers in the production of high-performance rigid rod polymers, for example, linear rigid oligoanthranilamides for electronic applications [Wu et al, *Organic Letters* (2004), 6(2), 229-232] and polypyridobisimidazoles and the like [see e.g. Beers et
30 al, *High-Performance Fibres* (2000), 93-155].

Existing processes to produce 2,5-dialkoxy- and 2,5-diarenoxyterephthalic acid involve stepwise alkylation of 2,5-dihydroxyterephthalic acid to form
35 the corresponding 2,5-alkoxy- and 2,5-

diarenoxyterephthalic esters followed by dealkylation of the ester to the acid. An n-hydroxy aromatic acid may be converted to an n-alkoxy aromatic acid by contacting the hydroxy aromatic acid under basic
5 conditions with an n-alkyl sulfate. One suitable method of running such a conversion reaction is as described in Austrian Patent No. 265,244. Yields are moderate to low, productivity is low and a two-step process is necessary.

10

A need therefore remains for a process by which ethers of aromatic acids can be produced economically and with high yields and high productivity in small- and large-scale operation, and in batch and
15 continuous operation.

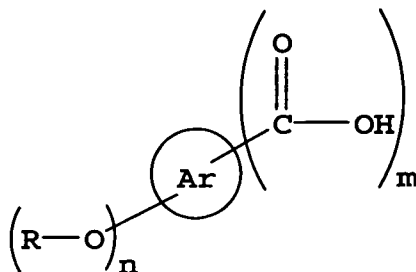
Summary

The inventions disclosed herein include
20 processes for the preparation of an ether of an aromatic acid, processes for the preparation of products into which such an ether can be converted, the use of such processes, and the products obtained and obtainable by such processes.

25

One embodiment of the processes hereof provides a process for preparing an ether of an aromatic acid, the ether being described by the structure of Formula I

30

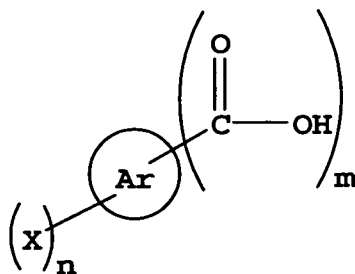


I

wherein Ar is a C₆~C₂₀ monocyclic or polycyclic aromatic nucleus, R is a univalent organic radical, n and m are
 5 each independently a nonzero value, and n+m is less than or equal to 8; comprising

(a) contacting a halogenated aromatic acid such as is described by the structure of Formula II

10



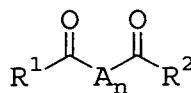
II

15 wherein each X is independently Cl, Br or I, and Ar, n and m are as set forth above, with

(i) a polar protic solvent, a polar aprotic solvent or an alcoholic solvent containing the alcoholate RO⁻M⁺ (wherein M is Na or K), wherein
 20 the polar protic solvent, polar aprotic solvent or alcoholic solvent is either ROH or is a solvent that is less acidic than ROH;

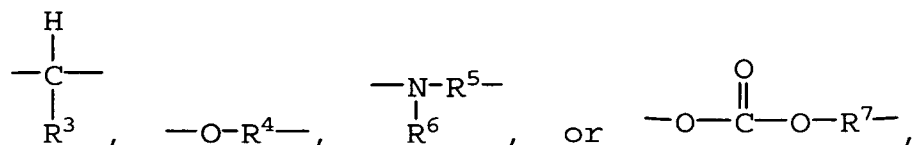
(ii) a copper (I) or copper (II) source; and

(iii) a diketone ligand that coordinates to copper, such as is described by the structure of
 25 Formula III



III

wherein A is



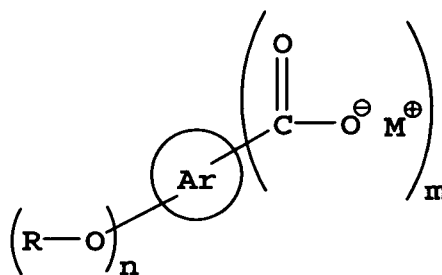
5

R^1 and R^2 are each independently selected from substituted and unsubstituted C_1 - C_{16} n-alkyl, iso-alkyl and tertiary alkyl groups; and
 10 substituted and unsubstituted C_6 - C_{30} aryl and heteroaryl groups;

R^3 is selected from H; substituted and unsubstituted C_1 - C_{16} n-alkyl, iso-alkyl and
 15 tertiary alkyl groups; substituted and unsubstituted C_6 - C_{30} aryl and heteroaryl groups; and a halogen;

R^4 , R^5 , R^6 and R^7 are each independently H or
 20 a substituted or unsubstituted C_1 - C_{16} n-alkyl, iso-alkyl or tertiary alkyl group; and $n = 0$ or 1;
 to form a reaction mixture;

(b) heating the reaction mixture to form the
 25 m-basic salt of the product of step (a), as described by the structure of Formula IV;



IV

- 5 (c) optionally, separating the Formula IV m-basic salt from the reaction mixture in which it is formed; and
- (d) contacting the Formula IV m-basic salt with acid to form therefrom an ether of an aromatic
- 10 acid.

Another embodiment of this invention provides a process for preparing a compound, monomer, oligomer or polymer by preparing an ether of an aromatic acid

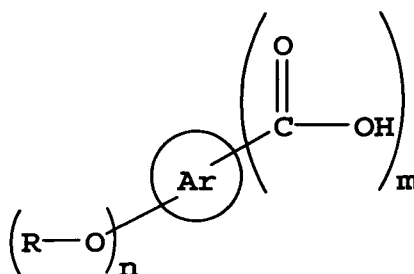
15 that is described generally by the structure of Formula I, and then subjecting the ether so produced to a reaction (including a multi-step reaction) to prepare therefrom a compound, monomer, oligomer or polymer.

20

Detailed Description

This invention provides a process having improved yield and productivity for preparing an ether of an aromatic acid, the ether being described by the

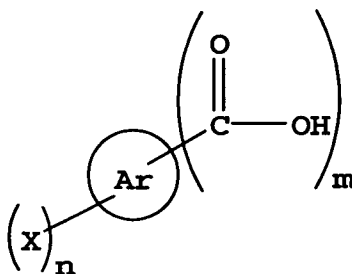
25 structure of Formula I



I

wherein Ar is a C₆~C₂₀ monocyclic or polycyclic aromatic
 5 nucleus, R is a univalent organic radical, n and m are
 each independently a nonzero value, and n+m is less
 than or equal to 8; comprising

One embodiment of the processes hereof
 10 proceeds by (a) contacting a halogenated aromatic acid
 such as is described by the structure of Formula II



II

15

wherein each X is independently Cl, Br or I, and Ar, n
 and m are as set forth above, with

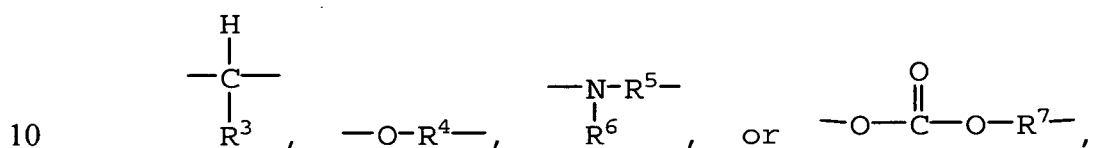
(i) a polar protic solvent, a polar aprotic
 20 solvent or an alcoholic solvent containing the
 alcoholate RO⁻M⁺ (wherein M is Na or K), wherein
 the polar protic solvent, polar aprotic solvent or
 alcoholic solvent is either ROH or is a solvent
 that is less acidic than ROH;

25 (ii) a copper (I) or copper (II) source; and

(iii) a diketone ligand that coordinates to copper, such as is described by the structure of Formula III



wherein A is

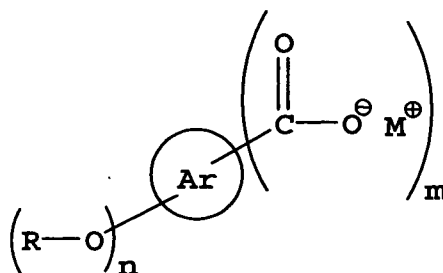


15 R^1 and R^2 are each independently selected from substituted and unsubstituted C_1 - C_{16} n-alkyl, iso-alkyl and tertiary alkyl groups; and substituted and unsubstituted C_6 - C_{30} aryl and heteroaryl groups;

20 R^3 is selected from H; substituted and unsubstituted C_1 - C_{16} n-alkyl, iso-alkyl and tertiary alkyl groups; substituted and unsubstituted C_6 - C_{30} aryl and heteroaryl groups; and a halogen;

25 R^4 , R^5 , R^6 and R^7 are each independently H or a substituted or unsubstituted C_1 - C_{16} n-alkyl, iso-alkyl or tertiary alkyl group; and $n = 0$ or 1; to form a reaction mixture;

30 (b) heating the reaction mixture to form the m-basic salt of the product of step (a), as described by the structure of Formula IV;



IV

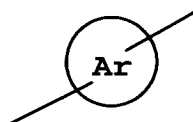
5 (c) optionally, separating the Formula IV m-basic salt from the reaction mixture in which it is formed; and

10 (d) contacting the Formula IV m-basic salt with acid to form therefrom an ether of an aromatic acid.

In Formulae I, II and IV, Ar is a C₆-C₂₀ monocyclic or polycyclic aromatic nucleus; n and m are each independently a nonzero value and n+m is less than or equal to 8; R is a univalent organic radical; and in Formula II, each X is independently Cl, Br or I.

The radical denoted by

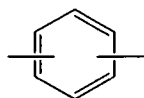
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is an n+m valent C₆-C₂₀ monocyclic or polycyclic aromatic nucleus formed by the removal of n+m hydrogens from different carbon atoms on the aromatic ring, or on the aromatic rings when the structure is polycyclic. The radical "Ar" may be substituted or unsubstituted; when unsubstituted, it contains only carbon and hydrogen.

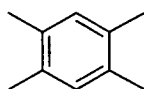
One example of a suitable Ar group is phenylene, as shown below, wherein $n=m=1$.

5



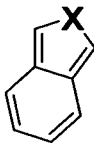
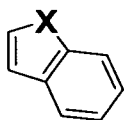
A preferred Ar group is shown below, wherein $n=m=2$.

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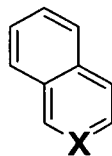
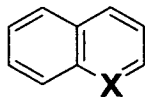
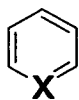


The univalent radical R is a univalent organic radical. Preferably, R is a C_1 - C_{12} alkyl group or an aryl group. More preferably, R is a C_1 - C_4 alkyl group or phenyl. Examples of particularly suitable R groups include without limitation methyl, ethyl, i-propyl, i-butyl, and phenyl. Several other nonlimiting examples of R are shown below:

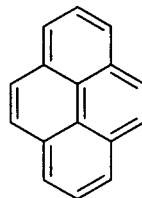
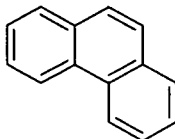
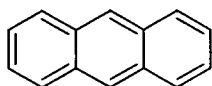
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$X = N, S$



$X = C, N$



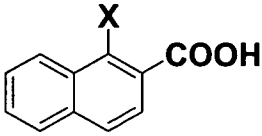
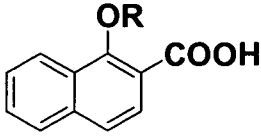
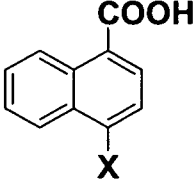
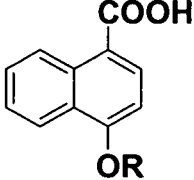
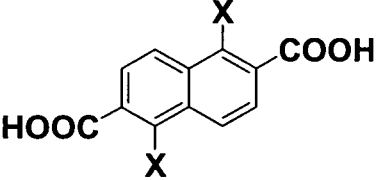
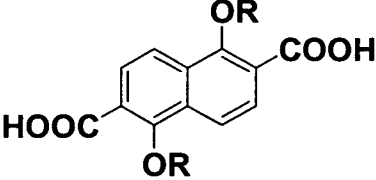
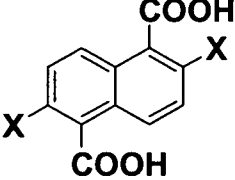
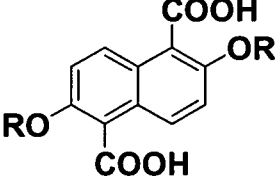
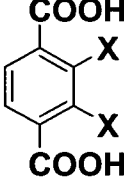
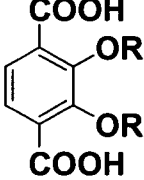
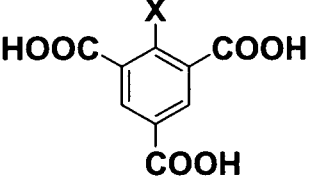
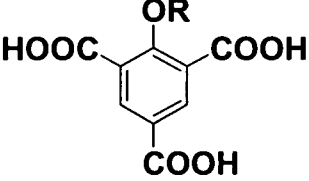
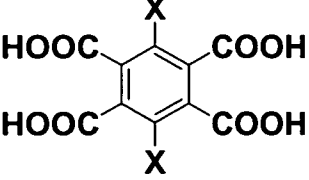
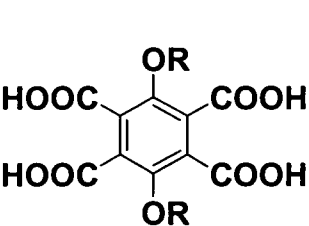
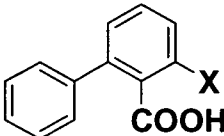
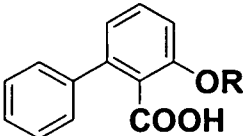
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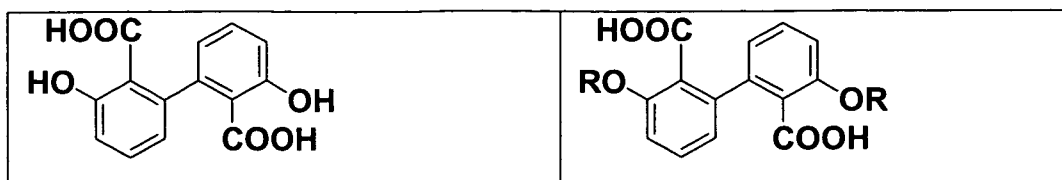
An "m-basic salt", as the term is used herein, is the salt formed from an acid that contains in each molecule m acid groups having a replaceable hydrogen atom.

5

Various halogenated aromatic acids, to be used as a starting material in the process of this invention, are commercially available. For example, 2-bromobenzoic acid is available from Aldrich Chemical
10 Company (Milwaukee, Wisconsin). It can be synthesized, however, by oxidation of bromomethylbenzene as described in Sasson et al, *Journal of Organic Chemistry* (1986), 51(15), 2880-2883. Other halogenated aromatic acids that can be used
15 include without limitation 2,5-dibromobenzoic acid, 2-bromo-5-nitrobenzoic acid, 2-bromo-5-methylbenzoic acid, 2-chlorobenzoic acid, 2,5-dichlorobenzoic acid, 2-chloro-3,5-dinitrobenzoic acid, 2-chloro-5-methylbenzoic acid, 2-bromo-5-methoxybenzoic acid, 5-
20 bromo-2-chlorobenzoic acid, 2,3-dichlorobenzoic acid, 2-chloro-4-nitrobenzoic acid, 2,5-dichloroterephthalic acid, 2-chloro-5-nitrobenzoic acid, 2,5-dibromoterephthalic acid, and 2,5-dichloroterephthalic acid, all of which are commercially available.
25 Preferably, the halogenated aromatic acid is 2,5-dibromoterephthalic acid or 2,5-dichloroterephthalic acid.

Other halogenated aromatic acids useful as a
30 starting material in the process of this invention include those shown in the left column of the table below, wherein X = Cl, Br or I, and wherein the corresponding ether of an aromatic acid produced therefrom by the process of this invention is shown in
35 the right column:

$(\text{COOH})_m\text{-Ar-(X)}_n$ I	$(\text{COOH})_m\text{-Ar-(OR)}_n$ II
	
	
	
	
	
	
	
	



In step (a), a halogenated aromatic acid is contacted with a polar protic or polar aprotic solvent or alcoholic solvent containing the alcoholate RO^-M^+ , wherein R is as defined above and M is Na or K; a copper (I) or copper (II) source; and a diamine ligand that coordinates to copper.

The alcohol may be ROH, which is preferred, or it may be an alcohol that is not more acidic than ROH. For example, if R is phenyl, such that ROH is phenol, then one nonlimiting example of a less acidic alcohol that can be used in step (a) is isopropanol. Examples of suitable alcohols include without limitation methanol, ethanol, i-propanol, i-butanol, and phenol, with the proviso that the alcohol is either ROH or an alcohol that is not more acidic than ROH.

The solvent may also be a polar protic or polar aprotic solvent or a mixture of protic or polar aprotic solvent. A polar solvent, as used herein, is a solvent whose constituent molecules exhibit a nonzero dipole moment. A polar protic solvent, as used herein, is a polar solvent whose constituent molecules contain an O-H or N-H bond. A polar aprotic solvent, as used herein, is a polar solvent whose constituent molecules do not contain an O-H or N-H bond. Examples of polar solvents other than an alcohol suitable for use herein include tetrahydrofuran, N-methylpyrrolidone, dimethylformamide, and dimethylacetamide.

In step (a), a halogenated aromatic acid is preferably contacted with a total of from about $n+m$ to $n+m+1$ equivalents of the alcoholate RO^-M^+ per equivalent of halogenated aromatic acid. Between m and $m+1$ equivalents is needed for forming the m -basic salt and between n and $n+1$ equivalents is needed for the displacement reaction. It is preferred that the total amount of alcoholate not exceed $m+n+1$. It is also preferred that the total amount of alcoholate not be less than $m+n$ in order to avoid reduction reactions. One "equivalent" as used in this context is the number of moles of alcoholate RO^-M^+ that will react with one mole of hydrogen ions; for an acid, one equivalent is the number of moles of acid that will supply one mole of hydrogen ions.

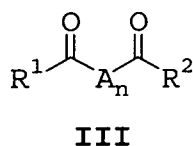
As mentioned above, in step (a), the halogenated aromatic acid is also contacted with a copper (I) or (II) source in the presence of a diketone ligand that coordinates to copper. The copper source and the ligand may be added sequentially to the reaction mixture, or may be combined separately (for example, in a solution of water or acetonitrile) and added together.

The copper source is a Cu(I) salt, a Cu(II) salt, or mixtures thereof. Examples include without limitation CuCl, CuBr, CuI, Cu₂SO₄, CuNO₃, CuCl₂, CuBr₂, CuI₂, CuSO₄, and Cu(NO₃)₂. The selection of the copper source may be made in relation to the identity of the halogenated aromatic acid used. For example, if the starting halogenated aromatic acid is a bromobenzoic acid, CuCl, CuBr, CuI, Cu₂SO₄, CuNO₃, CuCl₂, CuBr₂, CuI₂, CuSO₄, and Cu(NO₃)₂ will be included among the useful

choices. If the starting halogenated aromatic acid is a chlorobenzoic acid, CuBr, CuI, CuBr₂ and CuI₂ will be included among the useful choices. CuBr and CuBr₂ are in general preferred choices for most systems. The
 5 amount of copper used is typically about 0.1 to about 5 mol% based on moles of halogenated aromatic acid.

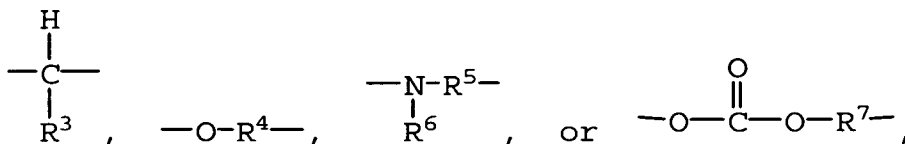
The ligand may be a diketone as described by the structure of Formula III

10



wherein A is

15



R¹ and R² are each independently selected from substituted and unsubstituted C₁-C₁₆ n-alkyl, iso-alkyl
 20 and tertiary alkyl groups; and substituted and unsubstituted C₆ - C₃₀ aryl and heteroaryl groups;

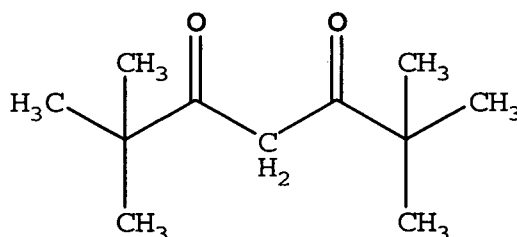
R³ is selected from H; substituted and unsubstituted C₁-C₁₆ n-alkyl, iso-alkyl and tertiary
 25 alkyl groups; substituted and unsubstituted C₆ - C₃₀ aryl and heteroaryl groups; and a halogen;

R⁴, R⁵, R⁶ and R⁷ are each independently H or a substituted or unsubstituted C₁-C₁₆ n-alkyl, iso-alkyl
 30 or tertiary alkyl group; and

n = 0 or 1.

The term "unsubstituted", as used with reference to an alkyl or aryl group in a diketone as described above, means that the alkyl or aryl group contains no atoms other than carbon and hydrogen. In a substituted alkyl or aryl group, however, one or more O or S atoms may optionally be substituted for any one or more of the in-chain or in-ring carbon atoms, provided that the resulting structure contains no -O-O- or -S-S- moieties, and provided that no carbon atom is bonded to more than one heteroatom. In a preferred embodiment, R³ is H.

In one embodiment, a diketone suitable for use herein as the ligand is 2,2',6,6'-tetramethylheptanedione-3,5 (Formula V):



V

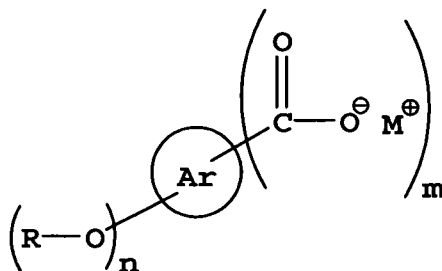
Other diketones suitable for use herein as the ligand include, without limitation, 2,4-pentanedione and 2,3-pentanedione.

A ligand suitable for use herein may be selected as any one or more or all of the members of the whole population of ligands described by name or structure above.

Various copper sources and ligands suitable for use herein may be made by processes known in the art, or are available commercially from suppliers such as Alfa Aesar (Ward Hill, Massachusetts), City Chemical
5 (West Haven, Connecticut), Fisher Scientific (Fairlawn, New Jersey), Sigma-Aldrich (St. Louis, Missouri) or Stanford Materials (Aliso Viejo, California).

In various embodiments, the ligand may be
10 provided in an amount of about 1 to about 8, preferably about 1 to about 2, molar equivalents of ligand per mole of copper. In those and other embodiments, the ratio of molar equivalents of ligand to molar
15 equivalents of halogenated aromatic acid may be less than or equal to about 0.1. As used herein, the term "molar equivalent" indicates the number of moles of ligand that will interact with one mole of copper.

In step (b), the reaction mixture is heated
20 to form the m-basic salt of the product of step (a), as described by the structure of Formula IV:



25

IV

The reaction temperature for steps (a) and (b) is preferably between about 40 and about 120°C,
30 more preferably between about 75 and about 95°C. Typically, the time required for step (a) is from about

0.1 to about 1 hour. The time required for step (b) is typically from about 0.1 to about 1 hour. Oxygen may be desirably excluded during the reaction. The solution is typically allowed to cool before optional
5 step (c) and before the acidification in step (d) is carried out.

The m-basic salt of the ether of the aromatic acid is then contacted in step (d) with acid to convert
10 it to the hydroxy aromatic acid product. Any acid of sufficient strength to protonate the m-basic salt is suitable. Examples include without limitation hydrochloric acid, sulfuric acid and phosphoric acid.

15 In one embodiment, the copper (I) or copper (II) source is selected from the group consisting of CuBr, CuBr₂ and mixtures thereof; the ligand is selected from the group consisting of 2,2',6,6'-tetramethylheptanedione-3,5, 2,4-pentanedione and 2,3-
20 pentanedione; and the copper (I) or copper (II) source is combined with two molar equivalents of the ligand.

The process described above also allows for effective and efficient synthesis of products made from
25 the resulting ethers of aromatic acids such as a compound, a monomer, or an oligomer or polymer thereof. These produced materials may have one or more of ester functionality, ether functionality, amide
functionality, imide functionality, imidazole
30 functionality, thiazole functionality, oxazole functionality, carbonate functionality, acrylate functionality, epoxide functionality, urethane functionality, acetal functionality, and anhydride
functionality.

35

Representative reactions involving a material made by the process of this invention, or a derivative of such material, include, for example, making a polyester from the ether of an aromatic acid and either diethylene glycol or triethylene glycol in the presence of 0.1% of $\text{Zn}_3(\text{BO}_3)_2$ in 1-methylnaphthalene under nitrogen, according to the method taught in US 3,047,536 (which is incorporated in its entirety as a part hereof for all purposes). Similarly, the ether of an aromatic acid is suitable for copolymerization with a dibasic acid and a glycol to prepare a heat-stabilized polyester according to the method taught in US 3,227,680 (which is incorporated in its entirety as a part hereof for all purposes), wherein representative conditions involve forming a prepolymer in the presence of titanium tetraisopropoxide in butanol at 200~250°C, followed by solid-phase polymerization at 280°C at a pressure of 0.08 mm Hg.

The ether of an aromatic acid can also be polymerized with the trihydrochloride-monohydrate of tetraaminopyridine in a condensation polymerization in strong polyphosphoric acid under slow heating above 100°C up to about 180°C under reduced pressure, followed by precipitation in water, as disclosed in US 5,674,969 (which is incorporated in its entirety as a part hereof for all purposes); or by mixing the monomers at a temperature from about 50°C to about 110°C, and then 145°C to form an oligomer, and then reacting the oligomer at a temperature of about 160°C to about 250°C as disclosed in U.S. Provisional Application No. 60/665,737, filed March 28, 2005 (which is incorporated in its entirety as a part hereof for all purposes), published as WO 2006/104974. The polymer that may be so produced may be a

pyridobisimidazole-2,6-diyl(2,5-dialkoxy-p-phenylene)
polymer or a pyridobisimidazole-2,6-diyl(2,5-
diareneoxy-p-phenylene) polymer such as a poly(1,4-
(2,5-diareneoxy) phenylene-2,6-pyrido[2, 3-d: 5,6-
5 d']bisimidazole) polymer. The pyridobisimidazole
portion thereof may, however, be replaced by any one or
more of a benzobisimidazole, benzobisthiazole,
benzobisoxazole, pyridobisthiazole and a
pyridobisoxazole; and the 2,5-dialkoxy-p-phenylene
10 portion thereof may be replaced by an alkyl or aryl
ether of one or more of isophthalic acid, terephthalic
acid, 2,5-pyridine dicarboxylic acid, 2,6-naphthalene
dicarboxylic acid, 4,4'-diphenyl dicarboxylic acid,
2,6-quinoline dicarboxylic acid, and 2,6-bis(4-
15 carboxyphenyl)pyridobisimidazole, wherein such an ether
is produced according to the methods disclosed herein.

The polymer prepared in such manner may, for
example, contain one or more of the following units:

20 pyridobisimidazole-2,6-diyl(2,5-dialkoxy-p-
phenylene) and/or pyridobisimidazole-2,6-diyl(2,5-
diphenoxy-p-phenylene) units;

units selected from the group consisting of
pyridobisimidazole-2,6-diyl(2,5-dimethoxy-p-phenylene),
25 pyridobisimidazole-2,6-diyl(2,5-diethoxy-p-phenylene),
pyridobisimidazole-2,6-diyl(2,5-dipropoxy-p-phenylene),
pyridobisimidazole-2,6-diyl(2,5-dibutoxy-p-phenylene)
and pyridobisimidazole-2,6-diyl(2,5-diphenoxy-p-
phenylene);

30 pyridobisthiazole-2,6-diyl(2,5-dialkoxy-p-
phenylene) and/or pyridobisthiazole-2,6-diyl(2,5-
diphenoxy-p-phenylene) units;

units selected from the group consisting of
pyridobisthiazole-2,6-diyl(2,5-dimethoxy-p-phenylene),
35 pyridobisthiazole-2,6-diyl(2,5-diethoxy-p-phenylene),

pyridobisthiazole-2,6-diyl(2,5-dipropoxy-p-phenylene),
pyridobisthiazole-2,6-diyl(2,5-dibutoxy-p-phenylene)
and pyridobisthiazole-2,6-diyl(2,5-diphenoxy-p-phenylene);

5 pyridobisoxazole-2,6-diyl(2,5-dialkoxy-p-phenylene) and/or pyridobisoxazole-2,6-diyl(2,5-diphenoxy-p-phenylene) units;

units selected from the group consisting of
pyridobisoxazole-2,6-diyl(2,5-dimethoxy-p-phenylene),
10 pyridobisoxazole-2,6-diyl(2,5-diethoxy-p-phenylene),
pyridobisoxazole-2,6-diyl(2,5-dipropoxy-p-phenylene),
pyridobisoxazole-2,6-diyl(2,5-dibutoxy-p-phenylene) and
pyridobisoxazole-2,6-diyl(2,5-diphenoxy-p-phenylene);

benzobisimidazole-2,6-diyl(2,5-dialkoxy-p-phenylene) and/or benzobisimidazole-2,6-diyl(2,5-
15 diphenoxy-p-phenylene) units;

units selected from the group consisting of
benzobisimidazole-2,6-diyl(2,5-dimethoxy-p-phenylene),
benzobisimidazole-2,6-diyl(2,5-diethoxy-p-phenylene),
20 benzobisimidazole-2,6-diyl(2,5-dipropoxy-p-phenylene),
benzobisimidazole-2,6-diyl(2,5-dibutoxy-p-phenylene)
and benzobisimidazole-2,6-diyl(2,5-diphenoxy-p-phenylene);

benzobisthiazole-2,6-diyl(2,5-dialkoxy-p-phenylene) and/or benzobisthiazole-2,6-diyl(2,5-
25 diphenoxy-p-phenylene) units;

units selected from the group consisting of
benzobisthiazole-2,6-diyl(2,5-dimethoxy-p-phenylene),
benzobisthiazole-2,6-diyl(2,5-diethoxy-p-phenylene),
30 benzobisthiazole-2,6-diyl(2,5-dipropoxy-p-phenylene),
benzobisthiazole-2,6-diyl(2,5-dibutoxy-p-phenylene) and
benzobisthiazole-2,6-diyl(2,5-diphenoxy-p-phenylene);

benzobisoxazole-2,6-diyl(2,5-dialkoxy-p-phenylene) and/or benzobisoxazole-2,6-diyl(2,5-
35 diphenoxy-p-phenylene) units; and/or

units selected from the group consisting of
benzobisoxazole-2,6-diyl(2,5-dimethoxy-p-phenylene),
benzobisoxazole-2,6-diyl(2,5-diethoxy-p-phenylene),
benzobisoxazole-2,6-diyl(2,5-dipropoxy-p-phenylene),
5 benzobisoxazole-2,6-diyl(2,5-dibutoxy-p-phenylene) and
benzobisoxazole-2,6-diyl(2,5-diphenoxy-p-phenylene)...

EXAMPLES

10 The advantageous attributes and effects of
the processes hereof may be seen in a laboratory
example, as described below. The embodiments of these
processes on which the example is based are
representative only, and the selection of those
15 embodiments to illustrate the invention does not
indicate that conditions, arrangements, approaches,
steps, techniques, configurations or reactants not
described in the example are not suitable for
practicing these processes, or that subject matter not
20 described in the example is excluded from the scope of
the appended claims and equivalents thereof.

As used herein, the term "conversion" refers
to how much reactant was used up as a fraction or
25 percentage of the theoretical amount. The term
"selectivity" for a product P refers to the molar
fraction or molar percentage of P in the final product
mix. The conversion multiplied by the selectivity thus
equals the maximum "yield" of P; the actual or "net"
30 yield will normally be somewhat less than this because
of sample losses incurred in the course of activities
such as isolating, handling, drying, and the like. The
term "purity" denotes what percentage of the in-hand,
isolated sample is actually the specified substance.

35

The meaning of abbreviations is as follows

"h" means hour(s), "mL" means milliliter(s), "g" means gram(s), "MeOH" means methanol, "mg" means milligram(s), "mmol" means millimole(s), and "mol equiv" means molar equivalent.

Example 1

In an air and moisture free environment, 4.2 g (77 mmol) of sodium methoxide is combined with 125 g of anhydrous methanol, followed by the addition of 5 g (15 mmol) of 2,5-dibromoterephthalic acid. Separately, 103 mg (0.03 mol equiv) of CuBr_2 and 0.06 mol equiv of 2,2',6,6'-tetramethylheptanedione-3,5 are combined under nitrogen, followed by addition of anhydrous methanol to dissolve. This solution is then added to form the reaction mixture. The reaction mixture is heated to reflux with stirring for 8 h, remaining under a nitrogen atmosphere. After cooling, the product is filtered, washed with hot MeOH and dried to yield a white solid as the bis-sodium salt. The isolated salt is then acidified with hydrochloric acid. The purity is over 95% and the net isolated yield is over 90%.

Each of the formulae shown herein describes each and all of the separate, individual compounds that can be formed in that formula by (1) selection from within the prescribed range for one of the variable radicals, substituents or numerical coefficients while all of the other variable radicals, substituents or numerical coefficients are held constant, and (2) performing in turn the same selection from within the prescribed range for each of the other variable radicals, substituents or numerical coefficients with the others being held constant. In addition to a selection made

within the prescribed range for any of the variable radicals, substituents or numerical coefficients of only one of the members of the group described by the range, a plurality of compounds may be described by selecting
5 more than one but less than all of the members of the whole group of radicals, substituents or numerical coefficients. When the selection made within the prescribed range for any of the variable radicals, substituents or numerical coefficients is a subgroup
10 containing (i) only one of the members of the whole group described by the range, or (ii) more than one but less than all of the members of the whole group, the selected member(s) are selected by omitting those member(s) of the whole group that are not selected to
15 form the subgroup. The compound, or plurality of compounds, may in such event be characterized by a definition of one or more of the variable radicals, substituents or numerical coefficients that refers to the whole group of the prescribed range for that
20 variable but where the member(s) omitted to form the subgroup are absent from the whole group.

Where a range of numerical values is recited
25 herein, the range includes the endpoints thereof and all the individual integers and fractions within the range, and also includes each of the narrower ranges therein formed by all the various possible combinations of those endpoints and internal integers and fractions
30 to form subgroups of the larger group of values within the stated range to the same extent as if each of those narrower ranges was explicitly recited. Where a range of numerical values is stated herein as being greater than a stated value, the range is nevertheless finite
35 and is bounded on its upper end by a value that is

operable within the context of the invention as described herein. Where a range of numerical values is stated herein as being less than a stated value, the range is nevertheless bounded on its lower end by a
5 non-zero value.

In this specification, unless explicitly stated otherwise or indicated to the contrary by the context of usage, amounts, sizes, ranges and other quantities
10 and characteristics recited herein, particularly when modified by the term "about", may but need not be exact, and may also be approximate and/or larger or smaller (as desired) than stated, reflecting tolerances, conversion factors, rounding off,
15 measurement error and the like, as well as the inclusion within a stated value of those values outside it that have, within the context of this invention, functional and/or operable equivalence to the stated value.

20

Where an embodiment of this invention is stated or described as comprising, including, containing, having, being composed of or being constituted by certain features, it is to be understood, unless the statement
25 or description explicitly provides to the contrary, that one or more features in addition to those explicitly stated or described may be present in the embodiment. An alternative embodiment of this invention, however, may be stated or described as
30 consisting essentially of certain features, in which embodiment features that would materially alter the principle of operation or the distinguishing characteristics of the embodiment are not present therein. A further alternative embodiment of this
35 invention may be stated or described as consisting of

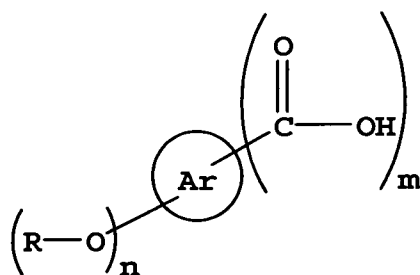
certain features, in which embodiment, or in insubstantial variations thereof, only the features specifically stated or described are present.

CLAIMS

5 What is claimed is:

1. A process for preparing an ether of an aromatic acid, the ether being described by the structure of Formula I

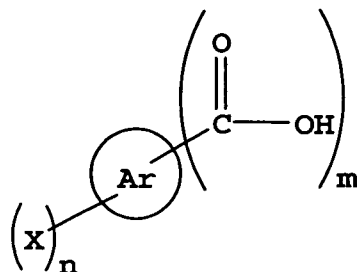
10



I

wherein Ar is a C₆-C₂₀ monocyclic or polycyclic aromatic
 15 nucleus, R is a univalent organic radical, n and m are
 each independently a nonzero value, and n+m is less
 than or equal to 8; comprising

(a) contacting a halogenated aromatic acid
 20 such as is described by the structure of Formula II



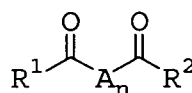
II

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wherein each X is independently Cl, Br or I, and Ar, n and m are as set forth above, with

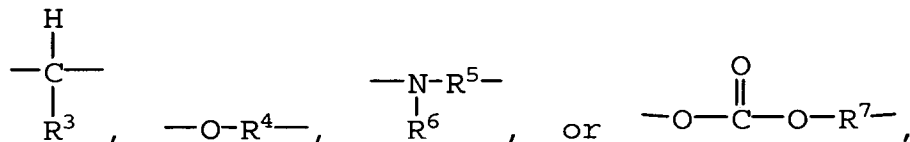
(i) a polar protic solvent, a polar aprotic solvent or an alcoholic solvent containing the alcoholate RO^-M^+ (wherein M is Na or K), wherein the polar protic solvent, polar aprotic solvent or alcoholic solvent is either ROH or is a solvent that is less acidic than ROH;

(ii) a copper (I) or copper (II) source; and
 (iii) a diketone ligand that coordinates to copper, such as is described by the structure of Formula III



III

wherein A is



20

R^1 and R^2 are each independently selected from substituted and unsubstituted C_1 - C_{16} n-alkyl, iso-alkyl and tertiary alkyl groups; and substituted and unsubstituted C_6 - C_{30} aryl and heteroaryl groups;

R^3 is selected from H; substituted and unsubstituted C_1 - C_{16} n-alkyl, iso-alkyl and tertiary alkyl groups; substituted and unsubstituted C_6 - C_{30} aryl and heteroaryl groups; and a halogen;

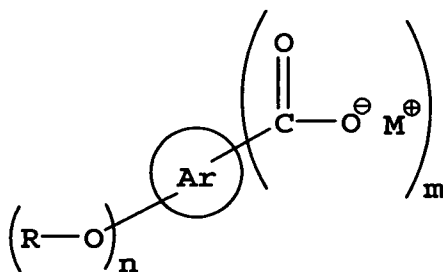
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R^4 , R^5 , R^6 and R^7 are each independently H or a substituted or unsubstituted C_1 - C_{16} n-alkyl, iso-alkyl or tertiary alkyl group; and $n = 0$ or 1;

5 to form a reaction mixture;

(b) heating the reaction mixture to form the m-basic salt of the product of step (a), as described by the structure of Formula IV;

10



IV

(c) optionally, separating the Formula IV m-basic salt from the reaction mixture in which it is formed; and

(d) contacting the Formula IV m-basic salt with acid to form therefrom an ether of an aromatic acid.

20

2. A process according to Claim 1 wherein the halogenated aromatic acid is selected from the group consisting of 2-bromobenzoic acid, 2,5-dibromobenzoic acid, 2-bromo-5-nitrobenzoic acid, 2-bromo-5-methylbenzoic acid, 2-chlorobenzoic acid, 2,5-dichlorobenzoic acid, 2-chloro-3,5-dinitrobenzoic acid, 2-chloro-5-methylbenzoic acid, 2-bromo-5-methoxybenzoic acid, 5-bromo-2-chlorobenzoic acid, 2,3-dichlorobenzoic acid, 2-chloro-4-nitrobenzoic acid, 2,5-dichloroterephthalic acid, 2-chloro-5-nitrobenzoic

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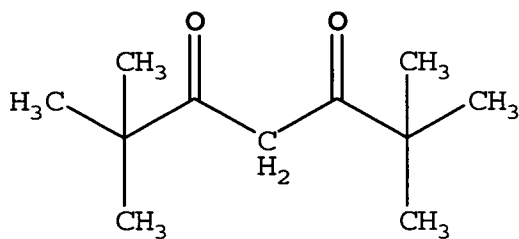
acid, 2,5-dibromoterephthalic acid, and 2,5-dichloroterephthalic acid.

3. A process according to Claim 1 wherein,
5 in step (a), a total of about $n+m$ to $n+m+1$ normal equivalents of RO^-M^+ are added to the reaction mixture per equivalent of the halogenated aromatic acid.

4. A process according to Claim 1 wherein
10 the copper source comprises a Cu(I) salt, a Cu(II) salt, or a mixture thereof.

5. A process according to Claim 4 wherein
the copper source is selected from the group consisting
15 of CuCl, CuBr, CuI, Cu₂SO₄, CuNO₃, CuCl₂, CuBr₂, CuI₂, CuSO₄, Cu(NO₃)₂, and mixtures thereof.

6. A process according to Claim 1 wherein
the ligand comprises 2,4-pentanedione, 2,3-pentanedione
20 or 2,2',6,6'-tetramethylheptanedione-3,5 (as shown by the structure below):



25

7. A process according to Claim 1 further comprising a step of combining the copper source with the ligand before adding them to the reaction mixture.

8. A process according to Claim 5 wherein
30 the copper source comprises CuBr or CuBr₂.

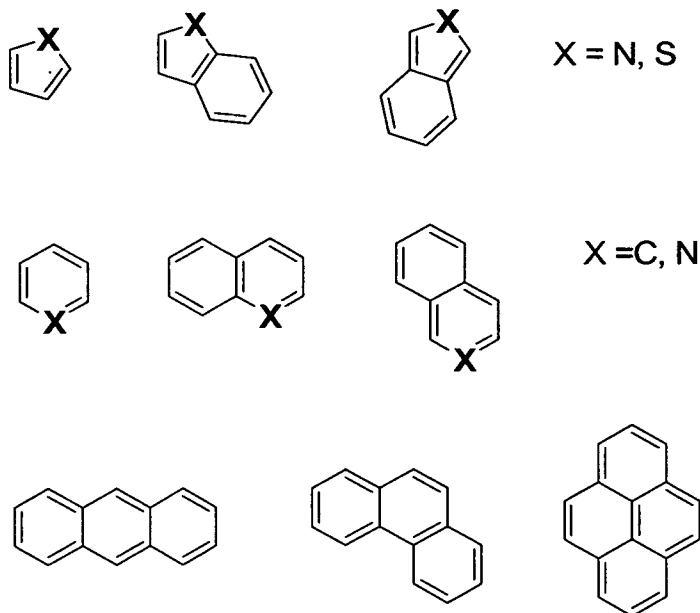
9. A process according to Claim 1 wherein copper is provided in an amount of between about 0.1 and about 5 mol% based on moles of halogenated aromatic acid.

5

10. A process according to Claim 1 wherein the ligand is provided in an amount of between about one and about two molar equivalents per mole of copper.

10 11. A process according to Claim 1 wherein R is selected from the group consisting of C₁-C₁₂ alkyl groups, aryl groups and the groups described by the structures of the following formulae:

15



12. A process according to Claim 11 wherein
20 R comprises a C₁-C₄ alkyl group or phenyl group.

13. A process according to Claim 1 wherein the alcoholic solvent comprises ROH.

14. A process according to Claim 1 wherein the halogenated aromatic hydroxy acid comprises 2,5-dibromoterephthalic acid or 2,5-dichloroterephthalic acid; R comprises methyl, ethyl, i-propyl, i-butyl or phenyl; the alcoholic solvent comprises ROH; the copper source comprises CuBr, CuBr₂, or a mixture of CuBr and CuBr₂; the copper source is provided in an amount of between about 0.1 and about 5 mol% based on moles of halogenated aromatic acid; the ligand comprises 2,2',6,6'-tetramethylheptanedione-3,5; and the ligand is provided in an amount of between about one and about two molar equivalents per mole of copper.

15. A process according to Claim 1 further comprising a step of subjecting the ether of the aromatic acid to a reaction to prepare therefrom a compound, monomer, oligomer or polymer.

16. A process according to Claim 15 wherein a polymer prepared comprises at least one member of the group consisting of pyridobisimidazole, pyridobisthiazole, pyridobisoxazole, benzobisimidazole, benzobisthiazole, and benzobisoxazole moieties.

17. A process according to Claim 16 wherein a polymer prepared comprises a pyridobisimidazole-2,6-diyl(2,5-dialkoxy-p-phenylene) polymer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/025917

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C51/367 C07C65/21

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, BEILSTEIN Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	BUCK E ET AL: "Ullmann diaryl ether synthesis: rate acceleration by 2,2,6,6-tetramethylheptane-3,5-dione" ORGANIC LETTERS, ACS, WASHINGTON, DC, US, vol. 4, no. 9, 2002, pages 1623-1626, XP002403679 ISSN: 1523-7060 the whole document	1-17
Y	JP 06 080609 A (NIPPON CHEMICAL IND) 22 March 1994 (1994-03-22) the whole document	1-17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

22 April 2008

Date of mailing of the international search report

02/05/2008

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2007/025917

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 6080609 A	22-03-1994	JP 3285391 B2	27-05-2002