SYNTHESIS OF ASYMMETRIC TETRACARBOXYLIC ACIDS AND CORRESPONDING DIANHYDRIDES

Inventor: Chun-Hua Chuang, Brecksville, OH (US)

Assignee: The United States of America as represented by the Administrator of the National Aeronautics and Space Administration, Washington, DC (US)

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U.S. Cl. 562/488; 562/491; 562/480; 562/887

Field of Classification Search None
See application file for complete search history.

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Primary Examiner—Karl J Puttlitz
Attorney, Agent, or Firm—Kent N. Stone; James V. Tura

ABSTRACT
This invention relates to processes for preparing asymmetrical biphenyl tetracarboxylic acids and the corresponding asymmetrical dianhydrides, namely 2,3,3',4'-biphenyl dianhydride (a-BPDA), 2,3,3',4'-benzophenone dianhydride (a-BTDA) and 3,4'-methylenediphthalic anhydride (-MDPA). By cross-coupling reactions of reactive metal substituted o-xylene derivatives in the presence of catalysts, this invention specifically produces asymmetrical biphenyl intermediates that are subsequently oxidized or hydrolyzed and oxidized to provide asymmetric biphenyl tetracarboxylic acids in comparatively high yields. These asymmetrical biphenyl tetracarboxylic acids are subsequently converted to the corresponding asymmetrical dianhydrides without contamination by symmetrical biphenyl dianhydrides.

30 Claims, No Drawings
SYNTHESIS OF ASYMMETRIC TETRACARBOXYLIC ACIDS AND CORRESPONDING DIANHYDRIDES

FIELD OF THE INVENTION

This invention relates to the synthesis of a series of asymmetric tetracarboxylic acids and the corresponding dianhydrides, namely, 2,3,3',4'-biphenyl dianhydride (a-BPDA), 2,3,3',4'-benzophenone dianhydride (a-BTDA), and 3,4'-methylendicarboxylic anhydride (a-MDPA). These tetracarboxylic acids and corresponding dianhydrides were prepared by cross-coupling of two asymmetrically substituted o-xylene or corresponding derivatives (Suzuki coupling) with various catalysts to form tetracarboxylic acids and the corresponding 2,3,3',4'-tetramethylbenzophenol and 2,3,3',4'-tetramethylbenzophenone. The asymmetrical tetramethylbenzophenol and the tetramethylenzenephirone were oxidized to obtain the corresponding tetracarboxylic acids which were then converted to 2,3,3',4'-benzophenone dianhydride and 2,3,3',4'-benzophenone dianhydride. In addition, the benzophenone tetracarboxylic acid can be hydrazide to 3,4'-methylene diphthalic tetracarboxylic acids which is converted to the corresponding 3,4'-methylendicarboxylic anhydride. The unique feature of this invention is that it allows the production of a series of asymmetric dianhydrides, not only a-BPDA, but also a-BTDA and a-MDPA. This capability of producing a-BPDA, a-BTDA and a-MDPA, will usher in innovation for the preparation of high Tg, low-melt viscosities and colorless polycydmids with interesting and novel properties for aerospace and electronic applications.

SUMMARY OF THE INVENTION

By employing a cross-coupling reaction (Suzuki coupling) with 3- and 4-substituted o-xylene in the presence of catalyst, this invention exclusively produces asymmetric precursors; namely, 2,3,3',4'-tetramethylbenzophenol and 2,3,3',4'-tetramethylbenzophenone. These asymmetric precursors are oxidized to a-BPDA and have more efficient processes for exclusively producing asymmetric 2,3,3',4'-biphenyl dianhydride (a-BPDA), 2,3,3',4'-benzophenone dianhydride (a-BTDA) and 3,4'-methylendicarboxylic anhydride (a-MDPA). The asymmetric 2,3,3',4'-biphenyl dianhydride (a-BPDA) has received more attention, because this dianhydride can produce polyimide resins having low-melt viscosities and higher glass-transition temperatures (Tg) than the symmetrical 3,3',4,4'-biphenyl dianhydride (s-BPDA).
prepreg process is labor intensive and expensive. Resin Transfer Molding (RTM) is a cost-effective approach to making components and has been successfully deployed with low-temperature polymers. U.S. Pat. No. 7,015,304 discloses preparation of polyimides with melt viscosities sufficiently low to enable RTM processing while maintaining stability and high temperature properties.

Accordingly, it is an object of this invention to provide processes for cross-coupling 3- and 4-substituted o-xylene and corresponding derivatives to produce asymmetric precursors which are subsequently oxidized to tetracarboxylic acids and then converted to the corresponding dianhydrides.

It is another object of this invention to provide processes for preparing asymmetrical tetracarboxylic acids and the corresponding dianhydrides useful in producing polyimides having lower-melt viscosities and high glass transition temperatures (Tg).

It is a further object of this invention to provide processes for the synthesis of a-BPDA and two additional dianhydrides a-BTDA and a-MDPA by cross-coupling substituted o-xylene to produce asymmetric precursors which are subsequently oxidized to the corresponding tetracarboxylic acids and then converted to the corresponding asymmetric dianhydrides in comparatively high yields.

These and other objects of this invention will become apparent from a further and more detailed description of the processes.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Recently, asymmetric 2,3,3',4'-biphenyl dianhydride (a-BPDA) has received more attention, because it can be used to produce polyimide resins having low-melt viscosities and high glass transition temperatures in comparison to the symmetrical 3,3',4,4'-biphenyl dianhydride (s-BPDA). In comparison, the prior art discloses a process for preparing a-BPDA by oxidative coupling of o-xylene or methyl o-phthalate with an organic acid salt of palladium under oxygen pressure to produce symmetrical and unsymmetrical intermediates which are oxidized and cyclodehydrated to obtain a mixture of a-BPDA and s-BPDA, followed by a process of which requires separating the two isomers.

The present invention exclusively provides processes for preparing asymmetrical tetracarboxylic acids and the corresponding dianhydrides, namely 2,3,3',4'-biphenyl dianhydride (a-BPDA), 2,3,3',4'-benzophenone dianhydride, (a-BTDA and 3,4'-methylenebisphthalic anhydride (a-MDPA), without the complex process of separating the isomers. By employing the cross-coupling of reactive metals such as magnesium (Mg), zinc (Zn) or lithium (Li) [Scheme 1] as well as the cross-reaction (Suzuki coupling) as shown in Scheme II and Scheme III using catalysts, alone or with co-catalysts or co-ligands, this invention specifically produces asymmetrical biphenyl intermediates that are subsequently hydrolyzed and oxidized or only oxidized to the asymmetric biphenyl tetracarboxylic acids. These asymmetrical biphenyl tetracarboxylic acids are converted to the corresponding asymmetrical dianhydrides either through cyclodehydration thermally or in the presence of an anhydride, without contamination of any symmetrical dianhydrides.

Scheme I of this invention illustrates the synthetic route via the active metal coupling of either substituted o-xylene (A) or 4-halophthalic anhydride or 4-halophthalimide (B) to afford the coupled intermediates of (D) and (E), which are oxidized or hydrolyzed and oxidized to form the tetracarboxylic acid (F), followed by dehydration e.g. with acetic anhydride to obtain the corresponding asymmetrical dianhydrides (G), which corresponds to 2,3,3',4'-biphenyl dianhydride (a-BPDA) when R is nil, and 3,4'-methylenebisphthalic anhydride (a-MDPA) when R is CH2.

As shown in the reactions of Scheme II, the asymmetric dianhydrides are obtained by cross-coupling o-xylene derivatives (I) and (II), if (I) is a 3-boron substituted o-xylene, then (II) is a 4-substituted o-xylene, or if (I) is a 4-boron substituted o-xylene, then (II) is a 3-substituted o-xylene derivative.
2,3,3',4'-biphenyl dianhydride (a-BPDA) is prepared by cross-coupling (I) and (II), where X is selected from the group consisting of Cl, Br, I, OSO₂CF₃, OSO₂CH₃ and Y is (OH)₂, or (OR)₂, where R is a lower alkyl group such as CH₃, C₂H₅, i-Pr, in order to form the asymmetrical 2,3,3',4'-tetramethylbiphenyl (III) in a common organic solvent, e.g. toluene, N,N-dimethylformamide (DMF), dimethoxyethane (DME), 1,4-dioxane, tetrahydrofuran (THF), anisole, or aqueous solution with phase transfer catalysts in the presence of palladium or nickel catalysts, either with or without a co-catalyst or co-ligands, such as Pd(PPh₃)₄, Pd(OAc)₂, Pd(PPh₃)₂Cl₂, PtCl₆(CH₃CN)₂, Pd(dba)₂/P(t-Bu)₂, Pd₄(dba)₂[t-Bu]₂, PF₆BF₄, NiCl₂(PPh₃)₂, NiCl₂(PC₃)₂, NiCl₂(dppe), NiCl₂(dpmb), and their corresponding polymer bound palladium or nickel catalysts.

Compound (III) is oxidized by potassium permanganate (KMnO₄), chromium trioxide (CrO₃), or by other oxidation methods such as low or high pressure nitric acid oxidation or by oxygen to form the 2,3,3',4'-biphenyl-tetracarboxylic acid (IV), which upon dehydration e.g. by acetic anhydride or thermal dehydration, yields 2,3,3',4'-biphenyl dianhydride (V). Alternatively, compounds (I) and (II) are cross-coupled with carbon monoxide gas in the presence of the Pd or nickel catalysts to form the asymmetrical 2,3,3',4'-tetramethylbenzophenone (VI), which is further oxidized e.g. by KMnO₄, CrO₃, low pressure nitric acid with oxygen, or with other known oxidation method to form 2,3,3',4'-benzophenonetetracarboxylic acid (VII) which is then dehydrated by acetic anhydride or thermally cyclodehydrated to yield 2,3,3',4'-benzophenone dianhydride (VIII). Alternatively, 2,3,3',4'-benzophenonetetracarboxylic acid (VIII) is reduced by hydrazine to form 3,4'-methylenediphthalic acid (IX), which upon dehydration e.g. by acetic anhydride yields 3,4'-methylenediphthalic anhydride (X).
In Scheme III, using catalysts described in Scheme II, a similar Suzuki cross-coupling reaction is carried out between 3- or 4-substituted boron-substituted o-xylene (1), boron-substituted phthalic derivative (1a), or boron-substituted phthalic diester (1b) and 4- or 3-halo-substituted phthalic anhydrides or phthalimidines (2), or diesters of phthalic acid respectively, to produce the coupled asymmetrical 4-(2,3-dimethylphenyl)phthalic anhydride or phthalimide (3). Compound (3) can be hydrolyzed e.g. by potassium hydroxide, followed by oxidation e.g. by KMnO₄, CrO₃ and other oxidizing methods such as low or high pressure nitric acid or with oxygen, to afford 2,3,3',4'-biphenyl tetracarboxylic acid (4), which upon dehydration e.g. with acetic anhydride or thermal cyclodehydration to yield 2,3,3',4'-biphenyl dianhydride (a-BPDA). In the presence of carbon monoxide gas, 2,3,3',4'-benzophenone dianhydride (10), (a-BTDA) is produced from compounds (7), (8) and (9) as shown in this reaction. Alternately, 2,3,3',4'-benzenophonentetra-carboxylic acid (9) is obtained through KMnO₄ oxidation of (2,3-dimethylphthalyl)-α-methylphthalic acid (12) after hydrolysis or from the corresponding phthalimide (11) via the Suzuki coupling of an o-xylene derivative (1) with α-halometaphthalic anhydride or α-halomethylphthalimide (2) with palladium or nickel catalysts. 2,3,3',4'-benzenophonentetra-carboxylic acid (9) can be reduced by hydrazine to 3,4'-methylene diphthalic acid (13), which upon dehydration yields 3,4'-methylene diphthalic anhydride (14) (a-MDPA).

In the cross-coupling reactions, X is selected from the group consisting of a halogen e.g. Cl, F, Br, I, or OSO₂CF₃ and OSO₂CH₃. Y is either (OH)₂ or (OR)₂. Z is either oxygen or nitrogen. R is —CH₃, —C=O, or nil. R' is a lower alkyl such as CH₃ or C₂H₅, and B is boron.

The following example illustrates a process for preparing the tetracarboxylic acids and corresponding dianhydrides using a process of this invention.

**EXAMPLE I**

**Synthesis of 4-(2,3-Dimethylphenyl)-N-methylphthalimide**

To a 250 ml 3-necked flask equipped with mechanical stirrer, 2,3-dimethylphenylboronic acid (10 g, 66.7 mmol), 4-bromo-N-phenylphthalimide (2) (14.44 g, 60 mmol), potassium carbonate (24.78 g, 180 mmol), a selected palladium catalyst (1.89 mmol) were added, along with 200 ml of dry dioxane. The heterogeneous reaction mixture was heated to 80-85°C under nitrogen overnight. The reaction mixture was filtered and concentrated to afford 10 g of the product. The aqueous solution was formed in the aqueous solution. The heterogeneous reaction mixture was extracted with ethyl acetate, dried over anhydrous magnesium sulfate, and then concentrated to induce crystallization of the desired product (8.1 gm, 60%).

**Synthesis of 2,3,3',4'-Biphenyltetracarboxylic acid (5)**

To a 250 ml 3-necked flask, 4-(2,3-dimethylphenyl) phthalic acid (16 g, 48.5 mmol) was added, then potassium hydroxide (5.4 g, 97 mmol) in 60 ml of water was added. The reaction mixture was warmed to 80°C and then potassium permanganate, KMnO₄ (~5 equiv.) was added as a solid in portion when the purple color disappeared periodically. The reaction mixture was allowed to proceed at 80°C until the purple color of KMnO₄ persisted for 30 min. The excess KMnO₄ was killed by ethanol and the precipitated MnO₂ was filtered off. The solvent was evaporated to dryness and the resulting residue was acidified to pH=1. The aqueous acidic solution was cooled in the refrigerator to induce crystallization. The solid was collected and dried to afford the desired product.

**Synthesis of 2,3,3',4'-Biphenyldianhydride (6)**

2,3,3',4'-Biphenyltetracarboxylic acid (4) (33 gm, 100 mmol) was suspended in minimum amount of acetic anhydride and heated to reflux for 4 hours. The reaction mixture was cooled to room temperature. The corresponding dianhydride precipitated out and was collected and washed with ether to remove trace of acetic acid before drying under vacuum to afford 26.5 g (90%) of a-BPDA. Mp=195-196°C.

**Synthesis of Asymmetrical 2,3,3',4'-Biphenyl Dianhydride (a-BPDA)**

![Diagram of the synthesis](image-url)
The dianhydrides prepared by the processes of this invention are particularly useful in preparing polyimides from one or more of a combination of reactants comprising dianhydrides selected from the group consisting of 2,3,3',4'-biphenyldianhydride (a-BPDA), 2,3,3',4'-benzophenone dianhydride (a-BTDA), and 3,4'-methylenediphthalic anhydride (a-MDPA), with at least one diamine and an endcap that can be melt-processed at temperatures between 232-270°C (450-520°F), without any solvent. The imide oligomers from this reaction have low-melt viscosities of 1-60 poise at 260-280°C. These imide oligomers are amenable to TRM, VARTM or resin infusion processes at 260-280°C, to product high quality polymer composites comprising carbon, glass, quartz or synthetic fibers for use at temperatures ranging up to about 550°F to 650°F.

An example of preparing the oligomers and polyimides using the asymmetric dianhydrides prepared by the processes of this invention is illustrated by the following reaction:
While this invention has been described by a number of specific examples, it is obvious that there are other variations and modifications that can be made without departing from the spirit and scope of the invention as set forth in the appended claims.

The invention claimed is:

1. Process for preparing asymmetrical tetracarboxylic acids which comprises cross-coupling a compound selected from the group consisting of:

\[ \text{H}_3\text{C} - \text{BY} \]

with a compound selected from the group consisting of:

\[ \text{COOR'} \]

and

\[ \text{COOR'} \]

in the presence of catalysts and additives to obtain a coupled intermediate having a formula selected from the group consisting of:

\[ \text{H}_3\text{C} - \text{BY} - \text{R'} \]

wherein R is nil, CH₂ or C=O, R' is a low alkyl group, Y is (OH)₂ or (OR')₂, Z is oxygen or nitrogen, X is selected from the group consisting of a halogen, OSO₂CF₃, and OSO₂CH₃, and B is boron; subsequently converting said intermediate to obtain tetracarboxylic acid selected from the group consisting of:

(a)

(b)
2. The process of claim 1 wherein palladium or nickel catalysts are present in the cross-coupling reaction.

3. The process of claim 1 wherein X is halogen and Y is (OH)₂, and the catalyst comprises palladium or nickel compounds.

4. The process of claim 1 wherein X is halogen, Y is (OR')₂, and the catalyst comprises palladium or nickel compounds.

5. The process of claim 1 wherein the 2,3,3',4'-biphenyl tetracarboxylic acid (a) is converted by dehydration into the corresponding 2,3,3',4'-biphenyl dianhydride having the formula:

6. The process of claim 1 wherein the 2,3,3',4'-biphenyl tetracarboxylic acid is converted to 2,3,3',4'-biphenyl dianhydride by dehydration with acetic anhydride.

7. The process of claim 1 wherein 3,4'-methylenediphthalic acid (b) is converted by dehydration into the corresponding 3,4'-methylenediphthalic anhydride having the formula:

8. The process of claim 1 wherein the 2,3,3',4'-benzophenone tetracarboxylic acid (c) is converted by dehydration into the corresponding 2,3,3',4'-benzophenone dianhydride having the formula:

9. The process of claim 1 wherein the substituted compound has the formula:

10. The process of claim 1 wherein the substituted compound has the formula:
in the presence of catalysts to yield the biphenyl intermediate having the formula:

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wherein R is nil, Y is (OH)$_2$, (OR)$_2$, or X is selected from the group consisting of a halogen, OSO$_2$CF$_3$, and OSO$_2$CH$_3$, and B is boron. R' is lower alkyl group; said intermediate subsequently hydrolyzed and oxidized to obtain biphenyl tetracarboxylic acid having the formula:

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12. The process of claim 1 wherein a compound has the formula:

wherein B is boron, Y is (OH)$_2$, (OR)$_2$, or X is selected from the group consisting of a halogen, OSO$_2$CF$_3$, and OSO$_2$CH$_3$, R' is lower alkyl group; said intermediate subsequently hydrolyzed to obtain biphenyl tetracarboxylic acid having the formula:

11. The process claim 1 wherein the substituted compound in the presence of catalysts to yield the biphenyl intermediate having the formula:

coupled with a phthalic ester to obtain compound having the formula:

wherein B is boron, Y is (OH)$_2$, (OR)$_2$, or X is selected from the group consisting of a halogen, OSO$_2$CF$_3$, and OSO$_2$CH$_3$, R' is lower alkyl group; said intermediate subsequently hydrolyzed to obtain biphenyl tetracarboxylic acid having the formula:

13. The process of claim 1 wherein a compound has the formula:

wherein R is nil, Y is (OH)$_2$, (OR)$_2$, or X is selected from the group consisting of a halogen, OSO$_2$CF$_3$, and OSO$_2$CH$_3$, and B is boron halogen, R' is lower alkyl group;
16. The process claim 1 wherein, the substituted compound has the formula:

in the presence of catalysts to yield the biphenyl intermediate having the formula:

wherein R is nil, B is boron, Y is (OH)ₖ or (OR')ₖ, X is selected from the group consisting of a halogen, OSO₂CF₃ and OSO₂CH₃, Z is nitrogen or oxygen, R' is lower alkyl group; said intermediate subsequently hydrolyzed to obtain the biphenyl tetracarboxylic acid having the formula:

14. The process of claim 9 wherein 2,3,3',4'-biphenyl tetracarboxylic acid is converted by thermal or chemical dehydration to the corresponding 2,3,3',4'-biphenyl dianhydride (α-BPDA) having the formula:

15. The process of claim 9 wherein the biphenyl tetracarboxylic acid is dehydrated with acetic anhydride to the corresponding biphenyl dianhydride.

17. The process of claim 15 wherein the benzophenone tetracarboxylic acid (c) is reduced with hydrazine to 3,4'-methylenediphthalic acid having the formula:
18. Process for preparing asymmetrical benzophenone tetracarboxylic acids which comprises cross-coupling with a compound having the formula:

\[
\begin{align*}
H_3C & \quad \text{CH}_3 \\
& \quad \text{CH}_3 \\
\end{align*}
\]

with a compound having the formula:

\[
\begin{align*}
\text{XR} & \quad \text{CH}_2 \\
\text{XR} & \quad \text{COOR}' \\
\end{align*}
\]

in the presence of catalysts and carbon monoxide when R is nil; but without carbon dioxide when R is C=O, to obtain benzophenone intermediates having a formula:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

subsequently hydrolyzing and oxidizing said intermediate to obtain tetracarboxylic acid having the formula:

\[
\begin{align*}
\text{HOOC} & \quad \text{COOH} \\
\text{COOH} & \quad \text{COOH} \\
\end{align*}
\]

wherein R' is a low alkyl group, Y is (OH), or (OR)', Z is oxygen or nitrogen, X is selected from the group consisting of a halogen, OSO₂(CH₃), and B is boron.

19. The process claim 18 wherein the compound has the formula:

\[
\begin{align*}
\text{H}_3C & \quad \text{CH}_3 \\
\end{align*}
\]

 coupled in the presence of catalysts and carbon dioxide with a compound having the formula:

\[
\begin{align*}
\text{X} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

yields a coupled intermediate having the formula:

\[
\begin{align*}
\text{H}_3C & \quad \text{CH}_3 \\
\text{COOH} & \quad \text{COOH} \\
\end{align*}
\]

subsequent oxidized to obtain the tetracarboxylic acid having the formula:

\[
\begin{align*}
\text{HOOC} & \quad \text{COOH} \\
\text{COOH} & \quad \text{COOH} \\
\end{align*}
\]
20. The process claim 18 wherein the compound has the formula:

![Chemical structure](image)
coupled in the presence of catalysts with a compound having the formula:

![Chemical structure](image)
to obtain an coupled intermediate having a formula:

![Chemical structure](image)
wherein B is boron, Y is (OH), or (OR)', X is halogen, R is C=O; said intermediate subsequently oxidized to afford benzophenone tetracarboxylic acid.

21. The process of claim 18 for preparing asymmetric tetracarboxylic acids which comprises cross-coupling a compound having the formula:

![Chemical structure](image)
coupled with a substituted phthalic ester having the formula:

![Chemical structure](image)
in the presence of catalysts to obtain intermediates having the formula:

![Chemical structure](image)
coupled with a substituted phthalimide having the formula:

![Chemical structure](image)
in the presence of catalysts to obtain an intermediate having the formula:

![Chemical structure](image)
wherein R is CH₃, R' is a low alkyl group, Y is (OH), or (OR)', X is selected from the group consisting of a halogen OSO₂CF₃, and OSO₂CH₃, and B is boron; said intermediate subsequently hydrolyzed and oxidized to obtain tetracarboxylic acid having the formula:

![Chemical structure](image)
wherein R is CH₃, or C=O, R' is a low alkyl group, Y is (OH), or (OR)', X is selected from the group consisting of a halogen OSO₂CF₃, and OSO₂CH₃, and B is boron, Z is oxygen or nitrogen; said subsequently hydrolyzed and oxidized to obtain tetracarboxylic acid having the formula:
with a compound having the formula:

23. The process claim 18 wherein the 2,3,3',4'-tetracarboxylic acid is converted by dehydration into the corresponding 2,3,3',4'-benzophenone dianhydride having the formula:

24. The process of claim 18 wherein the 2,3,3',4'-benzophenone tetracarboxylic acid is converted to 2,3,3',4'-benzophenone dianhydride by dehydration.

25. The process of claim 18 wherein 2,3,3',4'-benzophenone tetracarboxylic acid is converted to 2,3,3',4'-benzophenone dianhydride by dehydration with acetic anhydride.

26. The process of claim 18 wherein palladium or nickel catalysts are present in the cross-coupling reaction.

27. The process claim of 17 wherein the tetracarboxylic acid is converted by dehydration into the corresponding 3,4'-methylene diphthalic anhydride.

28. Process for preparing asymmetrical tetracarboxylic acids which comprises cross-coupling a substituted o-xylene having the formula:

29. The process of claim 28 wherein the tetracarboxylic acid is converted by dehydration into the corresponding dianhydride having the formula:

30. The process of claim 28 wherein M is a reactive metal selected from the group consisting of lithium, magnesium and zinc.

* * * *