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CATALYSEUR ACIDE IONIQUE LIQUIDE  
(54) Title: A METHOD OF MAKING AN ALKYLATED AROMATIC USING COMPOUND USING AN ACIDIC IONIC LIQUID  
CATALYST

(57) **Abrégé/Abstract:**

A process for alkylating an aromatic compound containing no hydroxyl groups comprising reacting at least one non-hydroxyl containing aromatic compound with at least one olefinic oligomer in the presence of an acidic ionic liquid catalyst, wherein the olefinic oligomer has a carbon range of from about C<sub>12</sub> to about C<sub>70</sub> and is synthesized by oligomerizing at least one monoolefin monomer in the presence of an acidic ionic liquid catalyst.



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(54) Title: A METHOD OF MAKING AN ALKYLATED AROMATIC USING COMPOUND USING AN ACIDIC IONIC LIQUID CATALYST

(57) Abstract: A process for alkylating an aromatic compound containing no hydroxyl groups comprising reacting at least one non-hydroxyl containing aromatic compound with at least one olefinic oligomer in the presence of an acidic ionic liquid catalyst, wherein the olefinic oligomer has a carbon range of from about C<sub>12</sub> to about C<sub>70</sub> and is synthesized by oligomerizing at least one monoolefin monomer in the presence of an acidic ionic liquid catalyst.



**WO 2007/143513 A3**

1       **A METHOD OF MAKING AN ALKYLATED AROMATIC USING COMPOUND**  
2                                   **USING AN ACIDIC IONIC LIQUID CATALYST**

3

4

FIELD OF THE INVENTION

5

6       The present invention is directed to a process for alkylating an aromatic compound  
7       containing no hydroxyl groups by reacting a non-hydroxyl containing aromatic compound  
8       with an olefinic oligomer in the presence of an acidic ionic liquid catalyst.

9

10

BACKGROUND OF THE INVENTION

11

12       It is well known to catalyze the alkylation of aromatics with a variety of Lewis or Bronsted  
13       acid catalysts. Typical commercial catalysts include phosphoric acid/kieselguhr, aluminum  
14       halides, boron trifluoride, antimony chloride, stannic chloride, zinc chloride, onium  
15       poly(hydrogen fluoride), hydrogen fluoride, acidic ionic exchange resins, acidic clays,  
16       synthetic or natural zeolites, and solid acids such as amorphous silica-alumina. Alkylation  
17       with lower molecular weight olefins, such as propylene, can be carried out in the liquid or  
18       vapor phase. For alkylations with higher olefins, such as C<sub>16+</sub> olefins, the alkylations are done  
19       in the liquid phase, often in the presence of hydrogen fluoride. Alkylation of benzene with  
20       higher olefins may be difficult, and typically requires hydrogen fluoride treatment. Such a  
21       process is disclosed by Himes in U.S. Patent No. 4,503,277, entitled "HF Regeneration in  
22       Aromatic Hydrocarbon Alkylation Process," which is hereby incorporated by reference for all  
23       purposes.

24

25       One problem with using acids, such as hydrogen fluoride, is that these acids are extremely  
26       corrosive, thus requiring special handling and equipment. Furthermore, the use of these acids  
27       might involve environmental problems. Another problem is that the use of these acids gives  
28       less desirable control of the precise chemical composition of the product.

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### DESCRIPTION OF THE RELATED ART

Ambler et al., U.S. Patent No. 5,304,615 discloses polymerizing an olefinic feedstock comprising one or more of butene-1, butene-2 and iso-butene by bringing the feedstock into contact with an ionic liquid.

Abdul-Sada et al., U.S. Patent No. 5,994,602 discloses a process for the alkylation of aromatics by reacting an aromatic hydrocarbon with an olefin in the presence of an ionic liquid.

### SUMMARY OF THE INVENTION

In its broadest embodiment, the present invention is directed to a non-hydroxyl containing alkyl aromatic compound wherein the alkyl substituent is derived from an olefinic oligomer having a carbon range of from about C<sub>12</sub> to about C<sub>70</sub> and wherein the oligomer is prepared by oligomerizing at least one monoolefin monomer in the presence of an acidic ionic liquid catalyst.

In another embodiment, the present invention is directed to a process for alkylating an aromatic compound containing no hydroxyl groups comprising reacting at least one non-hydroxyl containing aromatic compound with at least one olefinic oligomer in the presence of an acidic ionic liquid catalyst, wherein the olefinic oligomer has a carbon range of from about C<sub>12</sub> to about C<sub>70</sub> and is synthesized by oligomerizing at least one monoolefin in the presence of an acidic ionic liquid catalyst.

### DETAILED DESCRIPTION OF THE INVENTION

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications,

1 equivalents, and alternatives falling within the spirit and scope of the invention as defined by  
2 the appended claims.

3

4 Definitions

5

6 Olefins – The term “olefins” refers to a class of unsaturated aliphatic hydrocarbons having  
7 one or more carbon-carbon double bonds, obtained by a number of processes. The term  
8 “monoolefin” refers to olefins having one double bond. Alpha olefins are also included in the  
9 definition of olefins.

10

11 Alpha Olefins – The term “alpha olefins” refers to olefins that have a double bond between  
12 the first and second carbon atoms and are particularly reactive. Examples are 1-octene and 1-  
13 octadecene, which are used as the starting point for medium-biodegradable surfactants.  
14 Linear and branched olefins are also included in the definition of olefins.

15

16 Linear Olefins – The term “linear olefins,” which include normal alpha olefins and linear  
17 alpha olefins, refers to olefins which are straight chain, non-branched hydrocarbons with at  
18 least one carbon-carbon double bond present in the chain.

19

20 Double-Bond Isomerized Linear Olefins – The term “double-bond isomerized linear olefins”  
21 refers to a class of linear olefins comprising more than 5% of olefins in which the carbon-  
22 carbon double bond is not terminal (i.e., the double bond is not located between the first and  
23 second carbon atoms of the chain).

24

25 Partially Branched Linear Olefins – The term “partially branched linear olefins” refers to a  
26 class of linear olefins comprising less than one alkyl branch per straight chain containing the  
27 double bond, wherein the alkyl branch may be a methyl group or higher. Partially branched  
28 linear olefins may also contain double-bond isomerized olefins.

29

30 Branched Olefins – The term “branched olefins” refers to a class of olefins comprising one or  
31 more alkyl branches per linear straight chain containing the double bond, wherein the alkyl  
32 branch may be a methyl group or higher.

1 Non-Hydroxyl Containing Aromatic Compounds – The term “non-hydroxyl containing  
2 aromatic compounds” refers to aromatic compounds that do not have any hydroxyl groups  
3 either on the aromatic ring or on any substituent group(s).

4

5 Unsubstituted Aromatic Compounds – The term “unsubstituted compounds” refers to  
6 aromatic compounds that do not have any substituents attached to the aromatic ring(s). These  
7 compounds may be monocyclic, bicyclic or polycyclic. Examples of such compounds  
8 include, but are not limited to, benzene, naphthalene and the like.

9

10 Monosubstituted Aromatic Compounds – The term “monosubstituted compounds” refers to  
11 aromatic compounds that have one substituent attached to the aromatic ring. These  
12 compounds may be monocyclic, bicyclic or polycyclic. Examples of such compounds  
13 include, but are not limited to, aromatic compounds with one of the following substituents: -  
14 OR, -R, -X, -NH<sub>2</sub>, -NHR or -NR<sub>2</sub> and the like, wherein R is an alkyl group and X is a halide.

15

16 Disubstituted Aromatic Compounds – The term “disubstituted compounds” refers to aromatic  
17 compounds that have two substituents attached to the aromatic ring(s). The aromatic  
18 compounds may be monocyclic, bicyclic or polycyclic. Examples of such compounds  
19 include, but are not limited to, aromatic compounds with two substituents selected from the  
20 following: -OR, -R, -X, -NH<sub>2</sub>, -NHR or -NR<sub>2</sub> and the like, wherein R is an alkyl group and X  
21 is a halide.

22

23 Bronsted Acid – The term “Bronsted Acid” refers to a Lowry-Bronsted acid which is defined  
24 as a substance that gives up a proton. The strength of this acid depends upon its tendency to  
25 give up a proton. Substances that readily give up protons are typically strong acids. Sulfuric  
26 acid and hydrogen chloride are examples of strong Bronsted acids.

27

28 One embodiment of the present invention is a process for preparing an alkylated aromatic  
29 compound, wherein said process comprises reacting at least one aromatic compound with an  
30 olefinic oligomer, wherein the olefinic oligomer has a molecular weight of from about 160 to  
31 about 850 and is synthesized by oligomerizing an olefin in the presence of an acidic ionic  
32 liquid catalyst.

1 Aromatic Compound

2

3 At least one non-hydroxyl containing aromatic compound may be used for the alkylation  
4 reaction in the present invention. Specifically, the aromatic compound does not contain any  
5 hydroxyl groups either directly attached to the aromatic ring or on any of the substituents that  
6 are attached to the aromatic ring. Preferably the at least one aromatic compound comprises at  
7 least one of monocyclic aromatics, such as benzene, toluene, xylene - including all isomers  
8 (i.e., meta -, ortho- and para-), cumene or mixtures thereof. The at least one aromatic  
9 compound may also comprise bi-cyclic and poly-cyclic aromatic compounds, such as  
10 naphthalenes.

11

12 The aromatic compound may be an unsubstituted aromatic compound, a monosubstituted  
13 compound, and/or a disubstituted compound.

14

15 Sources of Aromatic Compound

16

17 The at least one aromatic compound employed in the present invention is prepared by  
18 methods that are well known in the art.

19

20 Olefinic Oligomer

21

22 The olefinic oligomer employed in this invention may be synthesized by reacting a low  
23 molecular weight monoolefin monomer in the presence of an acidic ionic liquid. The olefinic  
24 oligomer has a carbon range of from about C<sub>12</sub> to C<sub>70</sub>. Preferably, the olefinic oligomer is a  
25 propylene oligomer.

26

27 Monoolefin Monomer

28

29 The low molecular weight monoolefin monomer employed in this invention may be linear,  
30 isomerized linear, branched or partially branched linear olefins, or a mixture thereof.

31

1 The monoolefins may be derived from a variety of sources. Such sources include the normal  
2 alpha olefins from a normal alpha olefin process or an olefin metathesis process. Another  
3 source from which the olefins may be derived is through cracking of petroleum or Fischer-  
4 Tropsch wax. The Fischer-Tropsch wax may be hydrotreated prior to cracking. Other  
5 commercial sources include olefins derived from paraffin dehydrogenation, methanol-to-  
6 olefin processes (methanol cracker), and the like. Another source of olefins may be refinery  
7 olefins, such as those derived from a fluid catalytic cracker (FCC) unit. Another source of  
8 olefins may be those derived from Fischer-Tropsch synthesis.

9  
10 The monoolefins may also be substituted with other functional groups, such as carboxylic  
11 acid groups, heteroatoms, and the like, provided that such groups do not react with the acidic  
12 ionic liquid catalyst.

13

#### 14 Isomerized Normal Alpha Olefin Monomer

15

16 In one embodiment of the present invention the monoolefin employed is a normal alpha  
17 olefin. The normal alpha olefins may be isomerized using at least one of two types of acidic  
18 catalysts, solid or liquid. A solid catalyst preferably has at least one metal oxide and an  
19 average pore size of less than 5.5 angstroms. More preferably, the solid catalyst is a  
20 molecular sieve with a one-dimensional pore system, such as SM-3, MAPO-11, SAPO-11,  
21 SSZ-32, ZSM-23, MAPO-39, SAPO-39, ZSM-22 or SSZ-20. Other possible acidic solid  
22 catalysts useful for isomerization include ZSM-35, SUZ-4, NU-23, NU-87 and natural or  
23 synthetic ferrierites. These molecular sieves are well known in the art and are discussed in  
24 Rosemarie Szostak's Handbook of Molecular Sieves (New York, Van Nostrand Reinhold,  
25 1992) which is herein incorporated by reference for all purposes. A liquid type of  
26 isomerization catalyst that can be used is iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ).

27

28 The process for isomerization of normal alpha olefins may be carried out in batch or  
29 continuous mode. The process temperatures may range from about 50°C to about 250°C. In  
30 the batch mode, a typical method used is a stirred autoclave or glass flask, which may be  
31 heated to the desired reaction temperature. A continuous process is most efficiently carried

1 out in a fixed bed process. Space rates in a fixed bed process can range from 0.1 to 10 or  
2 more weight hourly space velocity.

3

4 In a fixed bed process, the isomerization catalyst is charged to the reactor and activated or  
5 dried at a temperature of at least 150°C under vacuum or flowing inert, dry gas. After  
6 activation, the temperature of the isomerization catalyst is adjusted to the desired reaction  
7 temperature and a flow of the olefin is introduced into the reactor. The reactor effluent  
8 containing the partially-branched, isomerized olefins is collected. The resulting partially-  
9 branched, isomerized olefins contain a different olefin distribution (i.e., alpha olefin, beta  
10 olefin; internal olefin, tri-substituted olefin, and vinylidene olefin) and branching content that  
11 the unisomerized olefin and conditions are selected in order to obtain the desired olefin  
12 distribution and the degree of branching.

13

14 Preferably, the monoolefin monomer is propylene, butene, isobutylene, pentene or mixtures  
15 thereof. More preferred, the monoolefin monomer is propylene. Typically, the monoolefin  
16 monomer has a carbon range of from about C<sub>2</sub>- C<sub>10</sub>. Preferably, the monoolefin monomer has  
17 a carbon range of from about C<sub>3</sub>-C<sub>5</sub>.

18

#### 19 Acidic Ionic Liquid Catalyst

20

21 The acidic ionic liquid catalyst is composed of at least two components which form a  
22 complex. The acidic ionic liquid catalyst in either the alkylation reaction or the olefin  
23 oligomerization process independently comprises a first component and a second component.  
24 The first component of the catalyst will typically comprise a Lewis Acidic compound  
25 selected from components such as Lewis Acidic compounds of Group 13 metals, including  
26 aluminum halides, alkyl aluminum halide, gallium halide, and alkyl gallium halide (see  
27 International Union of Pure and Applied Chemistry (IUPAC), version3, October 2005, for  
28 Group 13 metals of the periodic table). Other Lewis Acidic compounds besides those of  
29 Group 13 metals may also be used. Especially preferred for the first component is aluminum  
30 halide or alkyl aluminum halide. In particular, aluminum trichloride may be used as the first  
31 component for preparing the catalyst used in practicing the present invention.

32

1 The second component making up the ionic liquid catalyst is an organic salt or mixture of  
2 salts. These salts may be characterized by the general formula  $Q^+A^-$ , wherein  $Q^+$  is an  
3 ammonium, phosphonium, boronium, iodonium, or sulfonium cation and  $A^-$  is a negatively  
4 charged ion such as  $Cl^-$ ,  $Br^-$ ,  $ClO_4^-$ ,  $NO_3^-$ ,  $BF_4^-$ ,  $BCl_4^-$ ,  $PF_6^-$ ,  $SbF_6^-$ ,  $AlCl_4^-$ ,  $ArF_6^-$ ,  $TaF_6^-$ ,  $CuCl_2^-$   
5 ,  $FeCl_3^-$ ,  $SO_3CF_3^-$ ,  $SO_3C_7^-$ , and 3-sulfurtrioxyphenyl. Preferred for use as the second  
6 component are those quaternary ammonium halides containing one or more alkyl moieties  
7 having from about 1 to about 9 carbon atoms, such as, for example, trimethylamine  
8 hydrochloride, methyltributylammonium, and 1-butylpyridinium, or hydrocarbyl substituted  
9 imidazolium halides, such as for example, 1-ethyl-3-methyl-imidazolium chloride.

10

11 The presence of the first component should give the ionic liquid a Lewis or Franklin acidic  
12 character. Generally, the greater the mole ratio of the first component is to the second  
13 component, the greater the acidity of the ionic liquid mixture. When aluminum trichloride  
14 and trimethylamine hydrochloride are used as the first and second components, respectively,  
15 of the acidic ionic liquid catalyst, they preferably will be present in a mole ratio of from  
16 greater than about 1:1 to about 2:1.

17

18 Optionally, the acidic ionic liquid catalyst may comprise a third component. Preferably, the  
19 third component is a Bronsted acid. The Bronsted acid comprises hydrochloric acid (HCl),  
20 hydrobromic acid (HBr), trifluoromethanesulfonic acid, benzoic acid, para-toluene sulfonic  
21 acid, sulfuric acid and the like.

22

### 23 Preparation of Olefinic Oligomer

24

25 The olefinic oligomers employed in the present invention are synthesized by oligomerizing a  
26 low molecular weight monoolefin monomer in the presence of an acidic ionic liquid.  
27 Preferably the olefinic oligomer is selected from a propylene oligomer, a butene oligomer, an  
28 isobutylene oligomer, a pentene oligomer and mixtures thereof. Preferably, the olefinic  
29 oligomer is a propylene oligomer which is synthesized by oligomerizing propylene or  
30 isopropylene in the presence of an acidic ionic liquid. Preferably, the olefinic oligomer has a  
31 carbon range of from about 12 to about 60.

32

1 The olefin oligomer may be prepared by reacting the monoolefin monomer with the acidic  
2 ionic liquid catalyst, as described herein, in a continuous, batch or semi-batch reaction  
3 process at from about -20°C to about 100°C and a pressure of atmospheric pressure to about  
4 1000 psig. These process conditions are not limiting. Optimization of process conditions in  
5 the oligomerization of the olefin is within the scope of this invention.

6

7 Process for Preparing Alkylated Aromatic Compound

8

9 The alkylation process is carried out by charging a hydrocarbon feed comprising an aromatic  
10 compound or a mixture of aromatic compounds, an olefinic oligomer and an acidic ionic  
11 liquid catalyst to a reaction zone in which agitation is maintained. The acidic ionic liquid  
12 catalyst employed in the alkylation process may or may not be the same acidic ionic liquid  
13 catalyst employed in the olefinic oligomerization process. The resulting reaction mixture,  
14 which comprises the aromatic compound, the olefinic oligomer, and the acidic ionic liquid, is  
15 held in the alkylation zone under alkylation conditions for a time sufficient to allow  
16 substantial conversion (i.e., at least 80 mole% of the olefin has reacted) of the olefin to an  
17 aromatic alkylate. After a desired time, the reaction mixture is removed from the alkylation  
18 zone and fed to a liquid-liquid separator to allow hydrocarbon products to separate from the  
19 acidic ionic liquid catalyst. The acidic ionic liquid catalyst may be recycled to the reactor in a  
20 closed loop cycle. The hydrocarbon product is further treated to remove excess un-reacted  
21 aromatic compounds and optionally olefinic compounds from the desired alkylate product.  
22 The excess aromatic compounds are also recycled to the reactor.

23

24 Many types of reactor configurations may be used for the reactor zone. These include, but are  
25 not limited to, batch and continuous stirred tank reactors, reactor riser configurations,  
26 ebulating bed reactors, and other reactor configurations that are well known in the art. Many  
27 such reactors are known to those skilled in the art and are suitable for the alkylation reaction.  
28 Agitation is critical for the alkylation reaction and can be provided by rotating impellers, with  
29 or without baffles, static mixers, kinetic mixing in risers, or any other agitation devices that  
30 are well known in the art.

31

1 The alkylation process may be carried out at temperatures from about -10°C to about 100°C.  
2 The process is carried out under sufficient pressure that a substantial portion of the feed  
3 components remain in the liquid phase. Typically, a pressure of 0 to 1000 psig is satisfactory  
4 to maintain feed and products in the liquid phase.

5

6 The at least one aromatic compound or mixture of aromatic compounds and the olefinic  
7 oligomer may be injected separately into the reaction zone or may be mixed prior to injection.  
8 Both single and multiple reaction zones may be used with the injection of the aromatic  
9 compounds and the olefinic oligomer into one, several, or all reaction zones. The reaction  
10 zones need not be maintained at the same process conditions.

11

12 The charge mole ratio of the aromatic compound to the olefinic oligomer may range from  
13 about 0.5:1 to 100:1.

14

15 The alkylation process may be carried out in a batch or continuous process. The acidic ionic  
16 liquid catalyst may be recycled when used in a continuous process or batch process.

17

18 The olefinic oligomerization and alkylation processes may also take place in two separate  
19 reactors that are located in series. In the first reactor, the olefinic oligomerization takes place  
20 in accordance with the process steps described herein. The olefinic oligomerized product is  
21 then fed to a second reactor, wherein the alkylation process takes place in accordance with  
22 the process steps described herein.

23

24 The catalyst(s) used to make the olefinic oligomer and in the alkylation process may be  
25 recycled.

26

27 The product of the above-described olefin oligomerization and alkylation reactions is the  
28 non-hydroxyl containing alkylated aromatic compound herein.

29

30 Accordingly, another embodiment of the present invention is a non-hydroxyl containing  
31 alkylated aromatic compound wherein the alkyl substituent is derived from an olefinic  
32 oligomer having a carbon range of from about C<sub>12</sub> to C<sub>70</sub> and wherein the oligomer is

1 prepared by oligomerizing at least one monoolefin monomer in the presence of an acidic  
2 ionic liquid catalyst.

3

4 Other embodiments will be obvious to those skilled in the art.

5

6 The following examples are presented to illustrate specific embodiments of this invention and  
7 are not to be construed in any way as limiting the scope of the invention.

8

9

## EXAMPLES

10

11

### Example 1

12

#### Preparation of Tri-methyltributylammonium Chloroaluminate Ionic Liquid Catalyst

13

14 Anhydrous aluminum trichloride and methyltributylammonium chloride were dried  
15 overnight under vacuum at 100°C.

16

17 The preparation of the ionic liquid catalyst was carried out in a dry box. 550.6 grams of  
18 methyltributylammonium chloride was added to a beaker which was equipped with a  
19 magnetic stirring bar. 622.7 grams of anhydrous aluminum chloride was added to a  
20 second beaker. With the magnetic stirred activated, small portions of the solid aluminum  
21 chloride were slowly added to the beaker of methyltributylammonium chloride. As  
22 aluminum chloride was added, the heat of the reaction rose and the reaction mixture  
23 turned "pasty" and then turned partially liquid. The rate of addition of aluminum chloride  
24 was slowed to moderate the temperature increase in the beaker. As more aluminum  
25 chloride was added, more liquid was formed and eventually the reaction mixture began to  
26 stir freely. After the addition entire amount of aluminum trichloride, the reaction mixture  
27 was allowed to cool to ambient temperature and was stirred overnight. The next morning  
28 the reaction mixture was filtered through a sintered glass filter which had been dried at  
29 130 C. The final filtered ionic liquid catalyst was stored under nitrogen in a glass bottle.

1

2

Example 1a

3

Preparation of Trimethylammonium Chloroaluminate Ionic Liquid Catalyst

4

5 To a 1000 mL, dry, three neck glass round bottom flask fitted with a mechanical stirrer,  
6 thermometer and water cooled reflux condenser was added 67.2 grams (0.7 moles) of  
7 trimethylammonium hydrochloride. The hydrochloride salt was heated to 105°C under  
8 vacuum (400 mm Hg) for about 15 hours and then allowed to cool to room temperature  
9 under a nitrogen atmosphere. To the hydrochloride salt was added 187.8 grams (1.4  
10 moles) of aluminum trichloride in several portions under nitrogen over about 25 minutes  
11 while stirring and increasing the temperature of the flask 135°C. The contents of the flask  
12 were then heated to 70°C and stirred for 1 hour, 45 minutes and then cooled to room  
13 temperature under nitrogen. The product, liquid trimethylammonium chloroaluminate  
14 ionic liquid, was kept under nitrogen until use.

15

16

Example 2

17

Preparation of Propylene Oligomer

18

19 An 800 mL autoclave was purged with nitrogen. 30 mL of the ionic liquid catalyst as  
20 prepared in Example 1a and 20 mL of hexane were added to the autoclave by syringe. The  
21 autoclave was then evacuated for from about 30 to about 60 seconds to remove the nitrogen  
22 in the autoclave. The autoclave was then equilibrated at a temperature of from about 0°C to  
23 about 90°C while stirring. Propylene gas was added to a pressure of about 50 psig and was  
24 maintained at 50 psig over the reaction period. The reaction was run from about 1 hour to  
25 about 6 hours. The propylene feed was then disconnected from the autoclave and heating  
26 and/or cooling elements were removed. The autoclave was then vented to atmospheric  
27 pressure and opened. The hydrocarbon layer was decanted from the ionic liquid catalyst. The  
28 ionic liquid catalyst layer was then washed with hexane and the hexane layer was combined  
29 with the collected hydrocarbon from the reactor. The hydrocarbon layer was then stirred with  
30 water to remove any trace amounts of the ionic liquid catalyst. The hydrocarbon layer was  
31 then separated from the water and dried with magnesium sulfate (MgSO<sub>4</sub>). The propylene

1 oligomer product was isolated from the collected hydrocarbon layer by rotary evaporation  
2 taking place at 60°C to remove any volatile materials.

3

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Example 2a

5

Oligomerization of Propylene with Ionic Liquid in a Continuous Flow Reactor

6

7 A clean, dry, approximately 80 ml glass reactor equipped with a sintered glass frit gas inlet at  
8 the bottom and a magnetic stir bar and a needle vent was placed in a water bath heated on a  
9 magnetic stirring hot plate and equipped with a thermometer. The reactor was charged with  
10 approximately 10 ml of the ionic liquid of Example 1a and then approximately 25 ml of  
11 hexane. The water bath was cooled to between 0 and 7 °C with ice and propylene gas was  
12 introduced through the gas inlet and allowed to bubble through the ionic liquid at  
13 approximately 1.0 liters/minute over approximately 7 hours during which time the water bath  
14 was maintained between 40 and 51 °C.

15

16 The propylene gas flow was stopped and approximately 40 ml of hexane was added to the  
17 reactor. The reactor contents were then transferred to a separatory funnel and approximately  
18 10 gms of ice was added to the separatory funnel. The organic layer was washed with water,  
19 dried over anhydrous MgSO<sub>4</sub>, filtered and the hexane distilled under vacuum (approximately  
20 20 mm Hg) at approximately 80 °C to afford the oligomerized propylene. This reaction was  
21 repeated four times and the oligomerized propylene products from each were combined to  
22 yield approximately 260 grams of oligomerized propylene:  $MW_n = 769$ ,  $DI = 1.51$  by Size  
23 Exclusion Chromatography Multi Angle Light Scattering (MALS) analysis.

24

25

Example 2b

26

27

Oligomerization of Propylene with Ionic Liquid Catalyst in a Continuously Stirred Flow  
28 Reactor

29

30 To a clean, dry, approximately 1 liter, jacketed glass reactor equipped with a bottom drain  
31 valve and fitted with a mechanical paddle stirrer, thermometer, fritted glass glass inlet at the  
32 bottom of the reactor and a water cooled condenser fitted with a needle vent was added  
33 approximately 130 grams of Ionic Liquid catalyst of Example 1a and approximately 100 ml

1 of hexane. The stirrer was turned on at high speed and the reactor was cooled to between 10-  
2 16 °C and propylene gas was introduced through the gas dispersion tube at approximately 1  
3 liter/minute for approximately 1 hour and then lowered to between 0.4 – 0.6 liters/minute for  
4 approximately 7 hours while maintaining the reactor temperature between 23 and 36 °C. The  
5 propylene flow was stopped, the stirrer stopped and the the Ionic Liquid catalyst was drained  
6 from the reactor. Approximately 24 hours later, the following day, the Ionic Liquid catalyst  
7 was added back to the reactor, the stirrer started and propylene gas was introduced through  
8 the gas dispersion tube between 0.4 – 0.6 liters/minute for approximately 8 hours while  
9 maintaining the reactor temperature between 26 and 52 °C. The sequence of stopping the  
10 propylene gas, draining the Ionic Liquid catalyst and restarting the reaction approximately 24  
11 hours later was repeated twice and then the Ionic Liquid catalyst was drained from the  
12 reactor, the organic layer was isolated and washed with water, dried over anhydrous MgSO<sub>4</sub>,  
13 filtered and the hexane distilled under vacuum (approximately 20 mm Hg and 80 °C) to  
14 afford approximately 500 grams of oligomerized propylene: MW<sub>n</sub> = 917, DI = 1.34 by Size  
15 Exclusion Chromatography Multi Angle Light Scattering (MALS) analysis.

16

17

Example 2c

18 Oligomerization of Propylene Ionic Liquid Catalyst in a Continuously Stirred Flow Reactor

19

20 The reactor setup used in Example 2b was used except a slower stirring rate was used and the  
21 propylene gas was introduced at between 0.2-0.4 L/minute continuously over approximately  
22 52 hours. The Ionic Liquid catalyst of Example 1a was drained from the reactor, the organic  
23 layer was isolated and washed with water, dried over anhydrous MgSO<sub>4</sub>, filtered and the  
24 hexane distilled under vacuum (approximately 20 mm Hg and 80°C) producing  
25 approximately 460 grams of oligomerized propylene: MW<sub>n</sub> = 650, DI = 1.37 by Size  
26 Exclusion Chromatography Multi Angle Light Scattering (MALS) analysis.

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### Example 3

#### Alkylation of Toluene with Oligomerized Propylene with Ionic Liquid Catalyst

To a 100 mL, dry, three neck glass round bottom flask fitted with a mechanical stirrer, thermometer and water cooled reflux condenser was added 17.5 grams (0.189 moles) of toluene followed by 20.0 grams of oligomerized propylene, having a  $MW_n = 917$  and prepared according to the process of Example 2b, under nitrogen. To this stirring mixture was added approximately 2.0 grams of Methyl-tri-n-butylammonium aluminate ionic liquid, which was prepared according to the process of Example 1a, via syringe at room temperature in one portion. The temperature of the reaction mixture increased to  $59^\circ\text{C}$  within 5 minutes. The reaction product was then poured into approximately 50 grams of ice and washed with water, dried over anhydrous  $\text{MgSO}_4$ , filtered and the excess toluene was distilled under vacuum (approximately 20 mm Hg and  $80^\circ\text{C}$ ) to produce a yellow oil. The infrared spectrum of this oil showed weak bands at 705, 727, 756, 783 and  $815\text{ cm}^{-1}$  which is indicative of multiple substitution on the aromatic ring of toluene and strong bands at 1463 and  $1378\text{ cm}^{-1}$  which is indicative of polypropylene. Analysis of the product by mass spectroscopy (Time-of-Flight positive mode Field Ionization Mass Spectroscopy with temperature programmed probe inlet – 40 to  $500^\circ\text{C}$ ) showed the oil to be composed of a mixture of oligomerized propylene toluene alkylates (approximately 95%) by exact mass ranging in molecular weight from about 200 to 900 with the peak molecular weight around 260 and unreacted oligomerized propylene and paraffin (approximately 5%).

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### Example 4

#### Alkylation of ortho-xylene with Oligomerized Propylene with Ionic Liquid Catalyst

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The preparation of an ortho-xylene oligomerized propylene alkylate using an ionic liquid alkylation catalyst was performed in identical fashion to that of Example 3 except 20.1 grams (0.190 moles) of o-xylene was used in place of toluene. The temperature of the reaction increased to  $31^\circ\text{C}$  and the excess o-xylene was removed to produce a yellow oil. The infrared spectrum of this oil showed weak bands at about 817 and  $880\text{ cm}^{-1}$  characteristic of 1,2,4 substitution on an aromatic ring and strong bands at 1463 and  $1378\text{ cm}^{-1}$  indicative of polypropylene. Analysis of the product by mass spectroscopy (Time-of-Flight positive mode

- 1 Field Ionization Mass Spectroscopy and temperature programmed probe inlet – 40 to 500°C)
- 2 showed the oil to be composed of a mixture of oligomerized propylene xylenc alkylates
- 3 (approximately 95%) by exact mass ranging in molecular weight from about 200 to 600 with
- 4 the peak molecular weight around 330 and unreacted oligomerized propylene and
- 5 hydrocarbon (approximately 5%).

1 WHAT IS CLAIMED IS:

- 2
- 3 1. A process for alkylating an aromatic compound containing no hydroxyl groups
- 4 comprising reacting at least one non-hydroxyl containing aromatic compound with at
- 5 least one olefinic oligomer in the presence of an acidic ionic liquid catalyst, wherein
- 6 the olefinic oligomer has a carbon range of from about C<sub>12</sub> to about C<sub>70</sub> and is
- 7 synthesized by oligomerizing at least one monoolefin monomer in the presence of an
- 8 acidic ionic liquid catalyst.
- 9
- 10 2. The process according to Claim 1 wherein the at least one aromatic compound is
- 11 selected from unsubstituted aromatic compounds, monosubstituted aromatic
- 12 compounds, and disubstituted aromatic compounds.
- 13
- 14 3. The process according to Claim 2 wherein the at least one aromatic compound is
- 15 selected from benzene, toluene, meta- xylene, para-xylene, ortho-xylene, and mixtures
- 16 thereof.
- 17
- 18 4. The process according to claim 3, wherein the at least one aromatic compound is
- 19 toluene or ortho-xylene.
- 20
- 21 5. The process according to Claim 1 wherein the olefinic oligomer is selected from a
- 22 propylene oligomer, a butene oligomer, an isobutylene oligomer, a pentene oligomer,
- 23 an isopentene oligomer and mixtures thereof.
- 24
- 25 6. The process according to Claim 5 wherein the olefinic oligomer is a propylene
- 26 oligomer.
- 27
- 28 7. The process according to Claim 1 wherein the acidic ionic liquid catalyst in either the
- 29 alkylation reaction or the olefin oligomerization independently comprises a first
- 30 component and a second component, said first component comprising a compound
- 31 selected from the group consisting of aluminum halide, alkyl aluminum halide,
- 32 gallium halide, and alkyl gallium halide, and said second component comprising an

- 1           organic salt or mixtures thereof, wherein said organic salt is selected from an  
2           ammonium salt, a phosphonium salt, or a sulfonium salt.  
3
- 4    8.       The process according to Claim 7 wherein the acidic ionic liquid catalyst further  
5           comprises a Bronsted acid.  
6
- 7    9.       The process according to Claim 8 wherein the Bronsted acid comprises hydrochloric  
8           acid, hydrobromic acid, trifluoromethanesulfonic acid, benzoic acid, para-toluene  
9           sulfonic acid, sulfuric acid and the like.  
10
- 11  10.       The process according to Claim 9 wherein the Bronsted acid is hydrochloric acid.  
12
- 13  11.       The process according to Claim 7 wherein the first component is aluminum halide or  
14           alkyl aluminum halide.  
15
- 16  12.       The process according to Claim 11 wherein the first component is aluminum  
17           trichloride.  
18
- 19  13.       The process according to Claim 7 wherein said second component is selected from  
20           one or more of a hydrocarbyl substituted ammonium halide, hydrocarbyl substituted  
21           imidazolium halide, hydrocarbyl substituted pyridinium halide, alkylene substituted  
22           pyridinium dihalide, or hydrocarbyl substituted phosphonium halide.  
23
- 24  14.       The process according to Claim 13 wherein the second component is an alkyl  
25           substituted ammonium halide containing one or more alkyl moieties having from  
26           about 1 to about 9 carbon atoms.  
27
- 28  15.       The process according to Claim 14 wherein the second component comprises  
29           trimethylamine hydrochloride.  
30
- 31  16.       The process according to Claim 13 wherein the second component is an alkyl  
32           substituted imidazolium halide.

- 1
- 2 17. The process according to Claim 16 wherein the second component comprises at least  
3 1-ethyl-3-methyl-imidazolium chloride.  
4
- 5 18. The process according to Claim 7 wherein the first component is aluminum trichloride  
6 and the second component is trimethylammonium hydrochloride.  
7
- 8 19. The process according to Claim 7 wherein the acidic ionic liquid catalyst in both the  
9 alkylation reaction and the olefin oligomerization is the same.  
10
- 11 20. The process according to Claim 7 wherein the acidic ionic liquid catalyst in the  
12 alkylation reaction is different from the acidic ionic liquid catalyst in the olefin  
13 oligomerization process.  
14
- 15 21. The process according to Claim 1 wherein the acidic ionic liquid catalyst in the  
16 alkylation reaction is recycled.  
17
- 18 22. The process according to Claim 1 wherein the alkylation reaction takes place in a  
19 continuous process.  
20
- 21 23. A non-hydroxyl containing alkylated aromatic compound prepared by the process  
22 according to Claim 1.  
23
- 24 24. A non-hydroxyl containing alkylated aromatic compound wherein the alkyl  
25 substituent is derived from an olefinic oligomer having a carbon range of from about  
26 C<sub>12</sub> to C<sub>70</sub> and wherein the oligomer is prepared by oligomerizing at least one  
27 monoolefin monomer in the presence of an acidic ionic liquid catalyst.  
28
- 29 25. The non-hydroxyl containing alkylated aromatic compound according to Claim 24  
30 wherein the olefinic oligomer is selected from a propylene oligomer, a butene  
31 oligomer, an isobutylene oligomer, a pentene oligomer, an isopentene oligomer and  
32 mixtures thereof.

- 1
- 2 26. The non-hydroxyl containing alkylated aromatic compound according to Claim  
3 25, wherein the olefinic oligomer is a propylene oligomer.  
4
- 5 27. The non-hydroxyl containing alkylated aromatic compound according to Claim 24  
6 wherein the monoolefin monomer is selected from propylene, butene, isobutylene,  
7 pentene and mixtures thereof.  
8
- 9 28. The non-hydroxyl containing alkylated aromatic compound according to Claim 24  
10 wherein the acidic ionic liquid catalyst comprises a first component and a second  
11 component, said first component comprising a compound selected from the group  
12 consisting of aluminum halide, alkyl aluminum halide, gallium halide, and alkyl  
13 gallium halide, and said second component comprising a salt selected from an organic  
14 salt or mixtures thereof, wherein said organic is selected from an ammonium salt, a  
15 phosphonium salt, or a sulfonium salt.  
16
- 17 29. The non-hydroxyl containing alkylated aromatic compound according to Claim 28  
18 wherein the acidic ionic liquid catalyst further comprises a Bronsted acid.  
19
- 20 30. The non-hydroxyl containing alkylated aromatic compound according to Claim 29  
21 wherein the Bronsted acid comprises hydrochloric acid, hydrobromic acid, trifluoro  
22 methane sulfonic acid, benzoic acid, para-toluene sulfonic acid, sulfuric acid and the  
23 like.
- 24 31. The non-hydroxyl containing alkylated aromatic compound according to Claim 30  
25 wherein the Bronsted acid is hydrochloric acid.  
26
- 27 32. The non-hydroxyl containing alkylated aromatic compound according to Claim 28  
28 wherein the first component is aluminum halide or alkyl aluminum halide.  
29
- 30 33. The non-hydroxyl containing alkylated aromatic compound according to Claim 32  
31 wherein the first component is aluminum trichloride.  
32

- 1 34. The non-hydroxyl containing alkylated aromatic compound according to Claim 28  
2 wherein said second component is selected from one or more of a hydrocarbyl  
3 substituted ammonium halide, hydrocarbyl substituted imidazolium halide,  
4 hydrocarbyl substituted pyridinium halide, alkylene substituted pyridinium dihalide or  
5 hydrocarbyl substituted phosphonium halide.  
6
- 7 35. The non-hydroxyl containing alkylated aromatic compound according to Claim 34  
8 wherein the second component is an alkyl substituted ammonium halide containing  
9 one or more alkyl moieties having from about 1 to about 9 carbon atoms.  
10
- 11 36. The non-hydroxyl containing alkylated aromatic compound according to Claim 35  
12 wherein the second component comprises trimethylamine hydrochloride.  
13
- 14 37. The non-hydroxyl containing alkylated aromatic compound according to Claim 34  
15 wherein the second component is an alkyl substituted imidazolium halide.  
16
- 17 38. The non-hydroxyl containing alkylated aromatic compound according to Claim 37  
18 wherein the second component comprises at least 1-ethyl-3-methyl-imidazolium  
19 chloride.  
20
- 21 39. The non-hydroxyl containing alkylated aromatic compound according to Claim 28  
22 wherein the first component is aluminum trichloride and the second component is  
23 trimethylammonium hydrochloride.  
24
- 25 40. The non-hydroxyl containing alkylated aromatic compound according to Claim 24  
26 wherein the aromatic compound is selected from benzene, toluene, meta-xylene, para-  
27 xylene and ortho-xylene.  
28
- 29 41. The non-hydroxyl containing alkylated aromatic compound according to claim 40.  
30 wherein the aromatic compound is toluene or ortho-xylene.  
31