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(54) Title: CONVERTING LINEAR INTERNAL OLEFINS TO LINEAR ALPHA OLEFINS

(57) Abstract: Contacting a LIO with a borane isomerization catalyst in a reaction vessel to form a mixture that includes an adduct formed from the LIO and the borane isomerization catalyst, the adduct having an alkyl group bonded to boron at a non-terminal position of the alkyl group, isomerizing the adduct to move the alkyl group bonded to boron to a terminal position of the alkyl group, and dehydroborating the adduct in the presence of a scavenger olefin to form a LAO and a scavenger adduct that is formed from the scavenger olefin and the borane isomerization catalyst.

CONVERTING LINEAR INTERNAL OLEFINS TO LINEAR ALPHA OLEFINS

[001] This disclosure relates to methods for converting linear internal olefins to linear alpha olefins.

[002] Linear alpha olefins (LAOs) are used in production of plastics, fuels, nylons, pesticides, textiles, disinfectants, reagents, detergents, solvents, and others. Some current production methods produce LAOs via ethylene oligomerization of linear internal olefins (LIOs). However, conversion of LIOs to LAOs can be a challenging process due to the contrathermodynamic double bond isomerization involved in converting LIOs to LAOs.

[003] This disclosure provides a method for converting LIOs to LAOs including contacting a LIO with a borane isomerization catalyst in a reaction vessel to form a mixture that includes an adduct formed from the LIO and the borane isomerization catalyst, the adduct having an alkyl group bonded to boron at a non-terminal position of the alkyl group, isomerizing the adduct to move the alkyl group bonded to boron to a terminal position of the alkyl group, and dehydroborating the adduct in the presence of a scavenger olefin to form a LAO and a scavenger adduct that is formed from the scavenger olefin and the borane isomerization catalyst. Advantageously, the present disclosure does not employ a dehydroboration catalyst, such as cobalt or nickel, which are employed for some other processes.

[004] LIOs are linear olefins having from four carbons to twelve carbons including a double bond between two non-terminal carbons. Examples of LIOs include, but are not limited to, 2-butene, 2-methyl-2-butene, 2-pentene, 4-octene, 2-hexene, 3-hexene or a combination thereof. For example, a mixture including 4-octene and 2-butene may be employed.

[005] The method includes employing a borane isomerization catalyst that is selected from a group consisting of bis (trifluoromethyl)borane $[\text{HB}(\text{CF}_3)_2]$, dinitroborane $[\text{HB}(\text{NO}_2)_2]$, dicyanoborane $[\text{HB}(\text{CN})_2]$, bis (trichloromethyl)borane $[\text{HB}(\text{CCl}_3)_2]$, bis (1,1-difluorobenzyl) borane $[\text{HB}(\text{CF}_2\text{Ph})_2]$, bis (tribromomethyl)borane $\text{HB}(\text{CBr}_3)_2$, bis(pentafluorophenyl)borane [H-FAB], $\text{HB}(66\text{B6-F})$, $\text{HB}(656\text{-F})$, bis (2-

fluoro-2-propyl) borane [HB(CFMe₂)₂], duphenylaluminum [HAlPh₂], bis (4-trifluoromethylphenyl)borane [HB(p-CF₃-Ph)₂], dicyclohexylborane [HB(C₆H₁₁)₂], di-tert-butylborane [HB(tBu)₂], diphenylborane [HBPh₂], dimethylborane [HBMe₂], [dibromoborane HBBr₂], benzo tetrafluoroborole [HB(-CF₂-Ph-CF₂)], HB(66B6-F), HB(656-F) or a combination thereof. The borane isomerization catalyst can be part of an initial feedstock to the reaction vessel and/or can be recycled to the reaction vessel.

[006] The borane isomerization catalyst has a thermodynamically calculated activation energy for isomerizing an alkyl group from a non-terminal position (e.g., a secondary carbon) to a terminal position (e.g., a primary carbon) when bonded to a boron of an adduct, as discussed herein, in the range of from 1 kilocalories (kcal)/mole (mol) to 40 kcal/mol. In some embodiments, the borane isomerization catalyst has a ratio of boron at the primary carbon compared to boron bonded at an adjacent secondary carbon for a given reaction at equilibrium of greater than substantially 5.

[007] The method includes employing the LIO and the borane isomerization catalyst in a mole ratio in a range of from 1:1 to 50:1. For example, the LIO and the borane isomerization catalyst can be added to the reaction vessel in a mole ratio in a range of from 1:1 to 50:1 to form a mixture including the adduct from the LIO and the borane isomerization catalyst, the adduct having an alkyl group bonded to boron at a non-terminal position of the alkyl group. The LIO and the borane isomerization catalyst can form the adduct at a temperature in a range of from 10 °C to 30 °C. The mixture can include the LIO, the borane isomerization catalyst, and the adduct, among others for example.

[008] The method can include removing excess LIO from the mixture. Removing excess LIO can be accomplished by devolatilization, among other processes. Removing excess LIO can occur in another vessel (e.g., other than the reaction vessel). Removed excess LIO can be recycled to the reaction vessel.

[009] The method includes isomerizing the adduct to move the alkyl group bonded to boron to a terminal position of the alkyl group. For example, the contents of the reaction vessel can be heated to a temperature in a range of from 25 °C to 140 °C to move the alkyl group bonded to the boron to a terminal position of the alkyl group.

[010] The method includes dehydroborating the adduct in the presence of a scavenger olefin to form a LAO and a scavenger adduct that is formed from the scavenger olefin and the borane isomerization catalyst. Dehydroborating the adduct can occur in the reaction vessel and/or another vessel such as a falling film evaporator, for example. These scavenger adducts are useful for separating LAOs from the borane isomerization catalyst, for example.

[011] The scavenger olefin is any olefin capable of reacting with the adduct (e.g., when boron is at the terminal position of the adduct) to form the LAO and the scavenger adduct. For example, the scavenger olefin may be selected from a group consisting of cyclododecene, limonene, pinene, carene or a combination thereof. The reaction between the adduct and the scavenger olefin can be thermodynamically driven and/or driven by mass action (e.g., by selective removal of the LAO). The scavenger olefin may be employed in mole ratio in a range of from 0.5:1 to 10:1, where the mole ratio indicates the ratio of scavenger olefin to adduct, i.e. the adduct having the alkyl group bonded to boron to the terminal position of the alkyl group.

[012] LAOs are linear alpha olefins having from four carbons to twelve carbons. Examples of LAOs include, but are not limited, to 1-butene, 1-pentene, 1-octene, 1-hexene or a combination thereof. The LAOs are formed as the alkyl group bonded to the boron at the terminal position of the alkyl group is separated from the adduct. The scavenger adduct is formed by the scavenger olefin and the borane isomerization catalyst separated from the adduct.

[013] The method can include regenerating the borane isomerization catalyst from the scavenger adduct. The scavenger adduct can be heated to a temperature in a range of from 150 °C to 200 °C, to regenerate the borane isomerization catalyst (e.g., separate the borane isomerization catalyst and the scavenger olefin from the scavenger adduct). The method can include recycling the borane isomerization catalyst to the reaction vessel.

[014] Alternatively or in addition, the method can include removing a number of LAOs and substantially all of the scavenger adduct, collecting the number of LAOs from a distillation vessel, and/or recycling a portion of the number of LAOs as the one or more

reactants. For example, the method can include dimerizing a portion of the LAO to form a LIO and adding the formed LIO to the reaction vessel.

[015] The method can employ a solvent to form a solution including the LIO. Examples of solvents include, but are not limited to, benzene, cyclohexane, toluene or a combination thereof. For embodiments including the solvent, the solvent may be employed in a range of from greater than 0 weight percent to 85 weight percent, where the weight percent is based upon weight of the LIO and the solvent.

[016] The method can occur in one or more continuous flow reactors. Examples of continuous flow reactors include, but are not limited to, plug-flow reactors and fluidized bed reactors. Alternatively, and/or in addition, portions and/or all of the method can occur in one or more batch reactors.

[017] The following examples further illustrate the present disclosure in detail, but are not to be construed to limit the scope of the disclosure. All materials available from Sigma – Aldrich ®, unless otherwise noted. Use all materials without further purification, unless otherwise noted.

[018] Examples

[019] Prepare *bis*(pentafluorophenyl)borane (H-FAB) by metathesis of triethylsilane and tris(pentafluorophenyl)boron (FAB) as follows. Prepare a 3.25 wt% solution of FAB in ISOPAR™ E (100 g, 6.35 mmol, available from Exxon Mobil Chemical Co.) in a container. Add triethylsilane (370 mg, 3.17 mmol, 0.5 equivalent) to contents of the container while stirring. Heat contents of the container to 55 °C for 72 hours (hrs) and subsequently to 90 °C for 24 hrs. Remove volatile materials by vacuum. Dissolve non-volatile materials in heated toluene then to -40 °C. Filter to collect H-FAB. Wash H-FAB with pentane and dry in vacuum.

[020] Example (Ex) 1—Conversion of trans-4-octene to 1-octene.

[021] Mix H-FAB (0.12 mmol), cyclododecene (0.12 mmol), and cyclohexane-d₁₂ (0.7 mL, 20 µL of 1,2-difluorobenzene internal standard) in a reaction vessel at 23 °C. Add trans-4-octene (0.12 mmol) to the contents of the reaction vessel to contact trans-4-octene with H-FAB to form an adduct from the trans-4-octene and the H-FAB, the adduct has an alkyl group bonded to boron at a non-terminal position of the alkyl group, as

indicated by nuclear magnetic resonance (NMR) spectroscopy. NMR indicates approximately an 80% yield of the adduct. Isomerize the adduct by heating the contents of the reaction vessel to 60 °C for 10 hrs to move the alkyl group bonded to boron to a terminal position of the alkyl group and form 1-octyl-FAB. NMR indicates approximately a 90% yield of 1-octyl -FAB from the adduct.

[022] Dehydroboration of 1-octyl-FAB to 1-octene

[023] Mix 37 milligrams (mg) of 1-octyl-FAB (0.081 mmol), as prepared above, with approximately a stoichiometric amount limonene in a reaction vessel. Heat contents of reaction vessel to 60 °C for 2 hrs. NMR analysis indicates Ex. 2 (a scavenger adduct) forms from 1-octyl-FAB and limonene. NMR indicates a 45% yield of 1-octene.

[024] Ex 1 shows contacting a LIO with a borane isomerization catalyst in a reaction vessel forms 4-octyl-FAB, which isomerizes to 1-octyl-FAB. 1-octene is produced via dehydroboration of 1-octyl FAB in the presence of limonene.

WHAT IS CLAIMED IS:

1. A method for converting linear internal olefins (LIOs) to linear alpha olefins (LAOs), comprising:
 - contacting a LIO with a borane isomerization catalyst in a reaction vessel to form a mixture that includes an adduct formed from the LIO and the borane isomerization catalyst, the adduct having an alkyl group bonded to boron at a non-terminal position of the alkyl group;
 - isomerizing the adduct to move the alkyl group bonded to boron to a terminal position of the alkyl group; and
 - dehydroborating the adduct in the presence of a scavenger olefin to form a LAO and a scavenger adduct that is formed from the scavenger olefin and the borane isomerization catalyst.
2. The method of claim 1, wherein the LIO is selected from the group consisting of linear internal olefins having from four carbons to twelve carbons or a combination thereof.
3. The method of any one of the preceding claims wherein the borane isomerization catalyst is selected from the group consisting of *bis* (trifluoromethyl)borane [HB(CF₃)₂], dinitroborane [HB(NO₂)₂], dicyanoborane [HB(CN)₂], bis (trichloromethyl)borane [HB(CCl₃)₂], bis (1,1,difluorobenzyl) borane [HB(CF₂Ph)₂], bis (tribromomethyl)borane HB(CBr₃)₂, bis(pentafluorophenyl)borane [H-FAB], bis (2-fluoro-2-propyl) borane [HB(CFMe₂)₂], duphenylaluminum [HAlPh₂], bis (4-trifluoromethylphenyl)borane [HB(p-CF₃-Ph)₂], dicyclohexylborane [HB(C₆H₁₁)₂], di-tert-butylborane [HB(tBu)₂], diphenylborane [HBPh₂], dimethylborane [HBMe₂], [dibromoborane HBBr₂], benzo tetrafluoroborole [HB(-CF₂-Ph-CF₂)], HB(66B6-F), HB(656-F) or a combination thereof.
4. The method of any one of the preceding claims, wherein the LAO is selected from the group consisting of linear alpha olefins having from four carbons to twelve carbons or a combination thereof.

5. The method of any one of the preceding claims, wherein the scavenger olefin is selected from the group consisting of cyclododecene, limonene, pinene, carene or a combination thereof.
6. The method of any one of the preceding claims, including employing the LIO and the borane isomerization catalyst in a mole ratio in a range of from 1:1 to 50:1.
7. The method of any one of the preceding claims, including employing the scavenger olefin in mole ratio in a range of from 0.5:1 to 10:1, where the mole ratio indicates the ratio of scavenger olefin to the adduct having the alkyl group bonded to boron to a terminal position of the alkyl group.
8. The method of any one of the preceding claims, wherein method conditions include heating contents of the reaction vessel to a temperature in a range of from 25 °C to 140 °C.
9. The method of any one of the preceding claims, wherein dehydroborating the adduct in the presence of a scavenger olefin further includes separating the borane isomerization catalyst from the scavenger adduct by heating the scavenger adduct to a temperature in a range of from 150 °C to 200 °C to separate the scavenger olefin and the borane isomerization catalyst; and recycling the separated borane isomerization catalyst to the reaction vessel.
10. A scavenger adduct formed by the method of any one of the preceding claims.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/048431

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C5/25
ADD.
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 practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DANIEL J. PARKS ET AL: "Synthesis, Properties, and Hydroboration Activity of the Highly Electrophilic Borane Bis(pentafluorophenyl)borane, HB(C 6 F 5) ₂ ", ORGANOMETALLICS, vol. 17, no. 25, 1 December 1998 (1998-12-01), pages 5492-5503, XP055083837, ISSN: 0276-7333, DOI: 10.1021/om980673e table 2, entry 4 and corresponding description, page 5496	1-10
X	JP S62 223134 A (KUREHA CHEMICAL IND CO LTD) 1 October 1987 (1987-10-01) abstract ----- -/--	1-10

Further documents are listed in the continuation of Box C.

See patent family annex.

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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer O'Sullivan, Paul

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 874 507 A (EXXON RESEARCH ENGINEERING CO) 10 August 1961 (1961-08-10) page 1, line 11 - line 25 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/048431

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP S62223134 A	01-10-1987

GB 874507	A 10-08-1961	NONE	
