

PREPARATION, PURIFICATION, AND HYDROGENATION OF VINYLNORTRICYCLENE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 63/425,956, filed on November 16, 2022, which is incorporated by reference herein in its entirety.

TECHNICAL FIELD

[0002] This invention relates to synthesis of vinylnorbornene (VNTC) from ethylidene norbornene (ENB) and hydrogenation of VNTC into ethylnorbornene (h-VNTC).

BACKGROUND

[0003] Synthesis of vinylnorbornene (VNTC) has been accomplished from ethylidene norbornene (ENB) by a synthetic procedure involving the application of hazardous CS₂ and yielding less than 20% of VNTC based on the starting monomer. Another approach is one-step isomerization of ENB in the presence of alumina or alumina silicates and organic solvents. The catalyst-assisted isomerization typically requires the presence of an organic solvent and has a conversion of less than 40%. Hydrogenation of VNTC to h-VNTC by common catalyst systems at standard process temperatures typically results in the cleavage of the single C-C bond at the three-membered rings and formation of oligomers.

SUMMARY

[0004] This disclosure describes synthesis of vinylnorbornene (VNTC) from ethylidene norbornene (ENB) and its hydrogenation into ethylnorbornene (h-VNTC), in particular high-yield ENB to VNTC conversion, sufficient separation of VNTC from unreacted ENB, and selective hydrogenation of VNTC for the production of VNTC and h-VNTC at meaningful volumes for industrial applications. In some embodiments, the methods of the disclosure can advantageously include a solvent-free synthesis of vinylnorbornene (VNTC) from ethylidene norbornene (ENB). In some embodiments, the methods of the disclosure can advantageously include mild and less energy intensive reaction conditions (e.g., the reaction occurs at a temperature of less than 90°C).

[0005] The details of one or more embodiments of the subject matter of this disclosure are set forth in the accompanying drawings and the description. Other features, aspects, and

advantages of the subject matter will become apparent from the description, the drawings, and the claims.

BRIEF DESCRIPTION OF DRAWINGS

- [0006] FIG. 1A depicts a step in a scheme for synthesizing VNTC from ENB.
[0007] FIG. 1B depicts a step in a scheme for purifying VNTC from ENB.
[0008] FIG. 1C depicts a step in a scheme for hydrogenating VNTC into h-VNTC.

DETAILED DESCRIPTION

[0009] This disclosure describes the synthesis of vinylnorbornene (VNTC) from industrially accessible ethylidene norbornene (ENB), and, optionally, its hydrogenation into energy-rich ethylnorbornene (h-VNTC). The synthesis of VNTC disclosed herein can include a high-yield isomerization of ENB catalyzed by a heterogeneous catalyst, conversion of unreacted ENB into non-volatile compounds by Ring-Opening Metathesis Polymerization (ROMP), and subsequent distillation of VNTC. The hydrogenation of VNTC into h-VNTC can be accomplished under mild reaction conditions in order to prevent cleavage of the constrained three-member ring.

[0010] Provided herein are methods of synthesizing VNTC, wherein the methods include contacting ENB with an isomerization catalyst to yield a first mixture comprising ENB and VNTC, and separating vinylnorbornene from ethylidene norbornene of the first mixture to yield a second mixture, wherein the second mixture comprises at least about 90 mol% vinylnorbornene. The separating vinylnorbornene from ethylidene norbornene of the first mixture can include contacting the first mixture with a metathesis catalyst to yield a second mixture comprising the VNTC. In some embodiments, contacting the first mixture with a metathesis catalyst can yield a polymer formed from the ENB in the first mixture. The methods of the disclosure can further include separating the VNTC from the second mixture to yield a product mixture comprising VNTC. The methods of the disclosure can further include hydrogenating the VNTC to yield h-VNTC. For example, FIGS. 1A-1C depict steps in a scheme for synthesizing VNTC from ENB, purifying VNTC from excess ENB, and hydrogenating ENB into h-VNTC, respectively.

[0011] Using the synthetic method shown in FIG. 1A, a conversion of ENB to VNTC of about 58 mol% was demonstrated in the isomerization reaction of ENB, catalyzed by activated acidic alumina. The conversion was almost twice as high as compared to certain literature (30%) (*see, e.g.,* SU Application Publication No. 627,117 A1). Additionally, the

step disclosed in FIG. 1A does not require any solvents in contrast to previously described isomerization reactions. As used herein, “solvent” generally refers to a component in a reactant mixture other than a reactant, catalyst, or product. After the reaction is completed, the isomerization catalyst (e.g., alumina) can be easily removed by filtration to give the mixture of VNTC, ENB, and oligomeric products, and can optionally be reused for isomerizing a new portion of VNTC.

[0012] The step of contacting ENB with an isomerization catalyst yields a first mixture including ENB and VNTC (e.g., through the isomerization of ENB to VNTC). In some embodiments, contacting ENB with an isomerization catalyst can occur substantially solvent free. As used herein, “substantially solvent free” refers to the contacting ENB with an isomerization catalyst include less than 1 wt% solvent, less than 0.1 wt% solvent, or less than 0.01 wt% solvent. In some embodiments, contacting ENB with an isomerization catalyst can occur in the presence of a solvent. The solvent can include any suitable aprotic organic solvent, such as, acetone, acetonitrile, pentanes, hexanes, toluene, xylenes, dichloromethane, ethyl acetate, tetrahydrofuran, or the like.

[0013] The isomerization catalyst can include one or more of acidic alumina, a zeolite, zirconia, and titania. In some embodiments, the isomerization catalyst is a zeolite, zirconia, or titania. In some embodiments, the isomerization catalyst is acidic alumina. In some embodiments, the isomerization catalyst is acidic. As used here, the term “acidic alumina” refers to alumina that is adjusted to have a pH of less than 7 (e.g., a pH of about 6, about 5.5, about 5, about 4.5, about 4, about 3.5 or about 3). In some embodiments, the acidic alumina has an adjusted pH of about 4.5 ± 0.5 . The isomerization catalyst can be dried prior to its use in the contacting of ENB. In some embodiments, the acidic alumina can be dried at a temperature of at least about 50°C. For example, the acidic alumina can be dried at a temperature in a range of about 50°C to about 400°C, or about 100°C to about 300°C, or about 150°C to about 300°C, or about 200°C to about 250°C. The acidic alumina can be dried at reduced pressure. The acidic alumina can be dried for a time period of about 6 hours to about 10 days, or about 12 hours to about 5 days, or about 24 hours to about 72 hours, or about 48 hours. In some embodiments, the isomerization catalyst can include activated acidic alumina. The term “activated acidic alumina” refers to acidic alumina that has been dehydroxylated providing a highly porous material. In some embodiments, the isomerization catalyst can further include silica.

[0014] The step of contacting ENB with an isomerization catalyst can occur at a temperature in a range of about 0°C to about 400°C. For example, the temperature can be in a

range of about 35°C to about 400 °C, or about 100°C to about 300°C, or about 125°C to about 225°C, or about 150°C to about 200°C, or about 175°C to about 185°C, or about 180°C.

[0015] The step of contacting ENB with an isomerization catalyst can occur for about 2 hours to about 10 days. For example, the contacting ENB with an isomerization catalyst can occur for about 12 hours to about 5 days, or about 18 hours to about 4 days, or about 1 day to about 4 days, or about 36 hours to about 4 days, or about 3 days.

[0016] The step of contacting ENB with an isomerization catalyst can yield at least about 35 mol% VNTC. For example, the yield of VNTC can be at least about 40 mol%, at least about 45 mol%, at least about 50 mol%, at least about 55 mol%, or about 50 mol% to about 90 mol%, or about 50 mol% to about 75 mol%, or about 50 mol% to about 60 mol%, or about 55 mol% to about 60 mol%.

[0017] The methods of the disclosure can include separating vinylnorbornene from ethylidene norbornene of the first mixture to yield a second mixture, wherein the second mixture comprises at least about 90 mol% vinylnorbornene. The separating vinylnorbornene from ethylidene norbornene of the first mixture can include contacting the first mixture including ENB and VNTC with a metathesis catalyst to form a second mixture. The separation of VNTC from ENB and other miscellaneous side-products of the reaction of ENB with an isomerization catalyst can be achieved upon the conversion of ENB into a high molecular weight (M_w) non-volatile product upon the addition of a metathesis catalyst.

[0018] In some embodiments, the metathesis catalyst is a ring-opening metathesis polymerization (ROMP) catalyst. The methods disclosed here can include any suitable ROMP catalyst to one of ordinary skill in the art. For example, the ROMP catalyst can be a Grubbs Catalyst®, a Hoveyda-Grubbs catalyst®, or both. In some embodiments, the metathesis catalyst includes one or more of a Grubbs Catalyst®, a Hoveyda-Grubbs catalyst®, a Schrock type catalyst, a Ziegler-Natta catalyst, and a ROMP catalyst comprising one or more cyclic(alkyl)(amino) carbene ligands. In some embodiments, the ROMP catalyst includes one or more of a Schrock type catalyst, a Ziegler-Natta catalyst, and a ROMP catalyst comprising one or more cyclic(alkyl)(amino) carbene ligands. As used herein, the term “Schrock type catalyst” refers to a molybdenum(IV) or tungsten(IV) metal center with imido and alkoxide ligands, as well as an alkylidene ligand. In some embodiments, the ROMP catalyst includes a first generation Grubbs Catalyst®, a second generation Grubbs Catalyst®, a first generation Hoveyda-Grubbs catalyst®, a second generation Hoveyda-Grubbs catalyst®, or a third generation Grubbs catalyst®. In some embodiments, the ROMP

catalyst is a second generation Hoveyda-Grubbs catalyst®. In some embodiments, the methods of the disclosure include the addition of a second generation Hoveyda-Grubbs catalyst® to the first mixture including VNTC and ENB, which can result in the fast and exothermic ROMP of ENB. Without being bound by theory, it is thought that the high ring strain energy for ENB enables a faster metathesis reaction for endo-cyclic double C=C bond vs metathetical transformation for VNTC. The corresponding exothermic heat production can lead to temperatures of above 120°C. As a result, the metathesis catalyst can be thermally deactivated after the ROMP of ENB and does not induce significant metathesis dimerization for VNTC.

[0019] The metathesis catalyst can be immobilized by a template, e.g., to form a supported catalyst. For example, the metathesis catalyst can be covalently or datively bound to a surface, such as silica or a polymeric surface.

[0020] The metathesis catalyst can be provided in any suitable amount to an ordinary skilled artisan. For example, the metathesis catalyst can be provided in an amount of less than 5 wt%, less than 2 wt%, less than 1 wt%, less than 0.55 wt%, less than 0.1 wt%, less than 0.05 wt%, or less than 0.01 wt%, based on the total weight of the first mixture.

[0021] The step of contacting the first mixture with a metathesis catalyst can occur for 30 seconds to 1 hour or more. For example, contacting the first mixture with a metathesis catalyst can occur for about 1 minute to about 30 minutes, about 1 minute to 10 minutes, or about 1 minute to 5 minutes.

[0022] The methods of the disclosure can include contacting the first mixture with the metathesis catalyst via a drop-wise addition of the metathesis catalyst to the first mixture. In some embodiments, contacting the first mixture with the metathesis catalyst can occur in the presence of a solvent. The solvent can include any suitable aprotic organic solvent, such as, acetone, acetonitrile, pentanes, hexanes, toluene, xylenes, dichloromethane, ethyl acetate, tetrahydrofuran, or the like. In some embodiments, the metathesis catalyst is first dissolved in the solvent and then contacted with the first mixture (e.g., through drop-wise addition of the metathesis catalyst to the first mixture). In some embodiments, the metathesis catalyst is added in a solid state.

[0023] The methods of the disclosure can further include separating the VNTC from the second mixture to yield a product mixture including VNTC. In some embodiments, the product mixture can be substantially free of ENB (e.g., the product mixture has less than 5 mol% ENB, less than 2 mol% ENB, less than 1 mol% ENB, or less than 0.1 mol% ENB).

[0024] Separating the VNTC from the second mixture can include any suitable separation process or their combination to one of ordinary skill in the art, e.g., filtration, distillation, crystallization, chromatography, or the like. In some embodiments, separating the VNTC from the second mixture includes distilling the second mixture.

[0025] Distilling the second mixture can occur at a temperature in a range of about 50°C to about 200°C, or about 75°C to about 175°C, or about 125°C to about 150°C. In some embodiments, distilling the second mixture can occur at a temperature of about 125°C to about 150°C (e.g., about 139°C to about 142°C). In some embodiments, distilling the second mixture can occur at a pressure in a range of about 0.1 mTorr to about 760 Torr (e.g., about 1 mTorr to about 760 Torr, or about 1 Torr to about 760 Torr, or about 100 Torr to about 500 Torr).

[0026] The methods of the disclosure can further include hydrogenating the VNTC to yield h-VNTC. Hydrogenating the VNTC can include contacting the VNTC with a catalyst and H₂.

[0027] The catalyst can include a heterogeneous hydrogenation catalyst or a homogeneous hydrogenation catalyst. In some embodiments, the catalyst can include a metal, a metal oxide, or both. The catalyst can be one or more of NiO, Ni, Pd/C, Ru, Ru/C, Ru₂O₃, Ru/alumina, PdO, PtO₂, dichlorotris(triphenylphosphine)ruthenium(II), or cyclooctadiene rhodium(I) chloride. In some embodiments, the catalyst is PtO₂. In some embodiments, the catalyst can be any suitable single-site hydrogenation catalyst to one of ordinary skill in the art, for example, chloridotris(triphenylphosphine)rhodium(I). As used herein, the term “single-site hydrogenation catalyst” refers to a hydrogenation catalyst including a metal atom, ion, or small cluster of atoms (e.g., about 2 to about 10 atoms), held by surface ligands to a rigid framework.

[0028] The catalyst can be provided in any suitable amount to an ordinary skilled artisan. For example, the catalyst can be provided in an amount of less than 10 mol%, less than 5 mol%, less than 2 mol%, less than 1 mol%, less than 0.5 mol%, less than 0.1 mol%, or less than 0.05 mol%, based on the amount of mols of VNTC.

[0029] The hydrogenating can include H₂ as a gas and wherein, the H₂ is provided at a pressure of at least 25 psi. For example, the H₂ can be provided at a pressure of about 50 psi to about 250 psi, or about 100 psi to about 200 psi, or about 225 psi to about 275 psi. In some embodiments, the H₂ is provided at a pressure of about 225 psi to about 275 psi.

[0030] The hydrogenating can occur at a temperature of less than about 90°C. For example, the hydrogenating can occur at a temperature of less than about 90°C, or in a range of about 50°C to about 85°C, or about 65°C to about 85°C, or about 75°C.

[0031] The step of hydrogenating VNTC can occur for about 10 minutes to about 1 day. For example, hydrogenating VNTC can occur for about 30 minutes to about 12 hours, or about 1 hour to about 6 hours, about 1 hour to about 4 hours, or about 1 hour to about 3 hours.

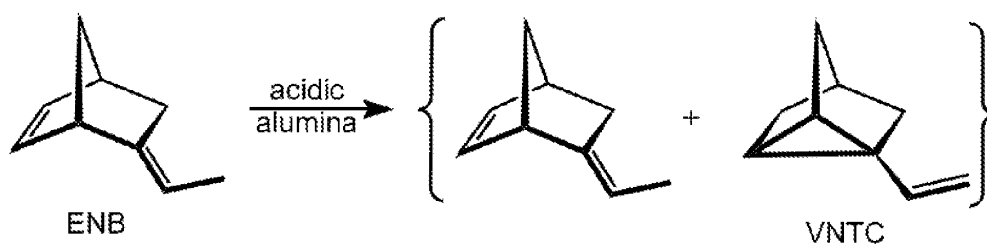
EXAMPLES

Example 1: Synthesis of VNTC

Catalyst Preparation.

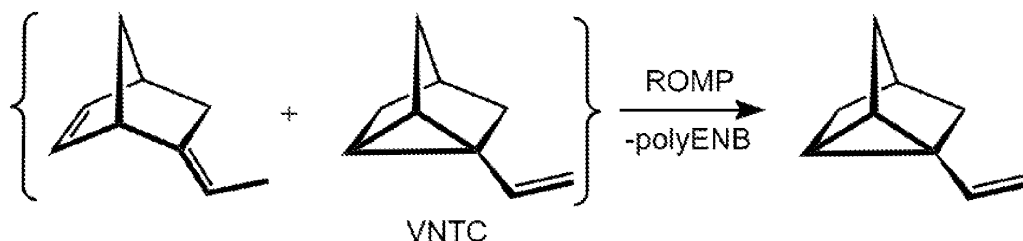
[0032] Acidic alumina was dried in a filled glass vessel (500 mL volume) in a vacuum oven for 48 hours at 225°C before being cooled and kept under nitrogen atmosphere.

Synthesis of VNTC.



[0033] 5-ethylidenebicyclo[2.2.1]hept-2-ene (ENB) (0.9 L, wherein ENB is provided as a mixture of isomers, 2:1 endo:exo) and 50 g of activated acidic alumina were stirred in a sealed pressure-resistant glass vessel at 180°C for 3 days to form a reaction mixture. The reaction mixture was cooled to the ambient temperature. The reaction mixture was filtered to filter out the alumina and a viscous liquid was obtained containing 58% of 1-vinyltricyclo[2.2.1.0^{2,6}]heptane (VNTC) according to ¹H NMR spectroscopy.

Purification by ROMP and Distillation.



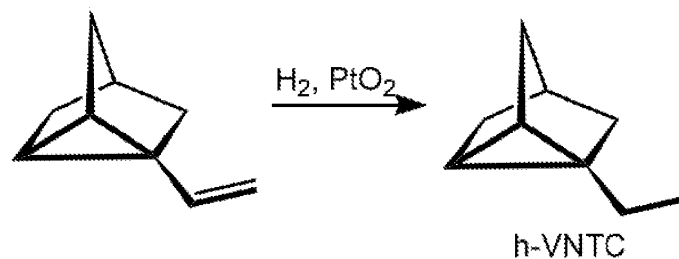
[0034] The reaction mixture of VNTC, ENB, and oligomeric products (2.5 L) was added to a 3L flask. A solution of ROMP catalyst (second generation Hoveyda-Grubbs Catalyst®, 200 mg) in 2 mL of dichloromethane was added dropwise to the flask under intense stirring. The temperature of the reaction mixture increased to 122°C in 2 min, and some gas evolution was observed. Under these reaction conditions, the catalyst was thermally deactivated and did not induce noticeable self-metathesis of VNTC. VNTC was then distilled from the reaction mixture at 139-142°C and ambient pressure to give 716 g of a liquid containing a pure product according to NMR spectroscopy. ¹H NMR (400 MHz, Benzene-*d*₆): δ 5.77 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.05 (d, *J* = 17.2 Hz, 1H), 4.94 (d, *J* = 10.4 Hz, 1H), 1.81 (s, 1H), 1.29 (s, 1H), 1.27 (s, 3H), 1.19 (s, 1H), 1.16 (s, 1H), 1.13 (s, 2H). ¹³C NMR (101 MHz, Benzene-*d*₆): δ 139.15, 109.95, 34.50, 33.86, 30.78, 26.93, 20.09.

Example 2: Hydrogenation of VNTC

Comparative Hydrogenation Experiments

[0035] Hydrogenation of VNTC with various catalysts including Pd/C (10 wt%), PtO₂ and Ni was attempted under process temperatures of about 90°C to about 200°C. The said reactions resulted in substantial degradation of the energy-rich VNTC core into hydrogenated ENB and oligomeric products. The higher temperatures induced the isomerization of VNTC into ENB.

Hydrogenation of VNTC



[0036] Parr Reactor (500 mL) was charged with VNTC (50 mL), obtained after distillation in Example 1, and PtO₂ (50 mg) under a nitrogen (N₂) atmosphere. Hydrogen gas was introduced to the system (150 psi) to form a reaction mixture, and the reaction mixture was heated at 75°C under intense mechanical stirring (about 400 rpm) for 2h. The reaction mixture was then filtered through a celite plug to form a mixture. The mixture consisted of about 82% 1-ethyltricyclo[2.2.1.0^{2,6}]heptane (h-VNTC) and about 18% 2-ethylbicyclo[2.2.1]heptane (h-ENB) according to ¹H NMR. ¹H NMR for h-VNTC (400 MHz,

Toluene-*d*₈): δ 1.90 (s, 1H), 1.53 (q, $J = 7.5$ Hz, 2H), 1.26 (dd, $J = 38.8, 9.3$ Hz, 4H), 1.12 (s, 2H), 0.90 (t, $J = 7.6$ Hz, 3H), 0.83 (s, 2H). ¹³C NMR (101 MHz, Toluene-*d*₈): δ 36.17, 33.96, 31.66, 24.15, 22.85, 15.94, 12.08.

[0037] Various embodiments of the features of this disclosure are described herein. However, it should be understood that such embodiments are provided merely by way of example, and numerous variations, changes, and substitutions can occur to those skilled in the art without departing from the scope of this disclosure. It should also be understood that various alternatives to the specific embodiments described herein are also within the scope of this disclosure.

[0038] Embodiment 1 is a method of synthesizing vinylnorbornene, the method comprising:

contacting ethylidene norbornene with an isomerization catalyst to yield a first mixture comprising ethylidene norbornene and vinylnorbornene; and
separating vinylnorbornene from ethylidene norbornene of the first mixture to yield a second mixture, wherein the second mixture comprises at least about 90 mol% vinylnorbornene.

[0039] Embodiment 2 is the method of embodiment 1, wherein separating vinylnorbornene from ethylidene norbornene of the first mixture comprises contacting the first mixture with a metathesis catalyst to yield the second mixture.

[0040] Embodiment 3 is the method of embodiment 1 or 2, further comprising separating the vinylnorbornene from the second mixture to yield a product mixture comprising vinylnorbornene.

[0041] Embodiment 4 is the method of embodiment 3, wherein separating the vinylnorbornene from the second mixture comprises distilling the second mixture.

[0042] Embodiment 5 is the method of embodiment 4, wherein distilling the second mixture occurs at a temperature in a range of about 50°C to about 200°C, or about 75°C to about 175°C, or about 125°C to about 150°C.

[0043] Embodiment 6 is the method of embodiment 4 or 5, wherein distilling the second mixture occurs at ambient pressure.

[0044] Embodiment 7 is the method of any one of embodiments 1-6, further comprising hydrogenating the vinylnorbornene to yield ethylnorbornene.

[0045] Embodiment 8 is the method of embodiment 7, wherein the hydrogenating comprises contacting the VNTC with a catalyst and H₂.

- [0046] Embodiment 9 is the method of embodiment 8, wherein the catalyst comprises a metal, a metal oxide, or both.
- [0047] Embodiment 10 is the method of embodiment 8 or 9, wherein the catalyst comprises NiO, Ni, Pd/C, Ru, Ru/C, Ru₂O₃, Ru/alumina, PdO, PtO₂, dichlorotris(triphenylphosphine)ruthenium(II), or cyclooctadiene rhodium(I) chloride.
- [0048] Embodiment 11 is the method of embodiment of claim 8, wherein the catalyst is a homogeneous catalyst.
- [0049] Embodiment 12 is the method of any one of embodiments 7-11, wherein the hydrogenating occurs at a temperature of less than about 90°C, or in a range of about 50°C to about 85°C, or about 65°C to about 85°C.
- [0050] Embodiment 13 is the method of any one of embodiments 7-12, wherein the hydrogenating comprises H₂ at a pressure of about 25 psi to about 250 psi, or about 100 psi to about 200 psi, or about 150 psi.
- [0051] Embodiment 14 is the method of any one of embodiments 7-13, wherein the hydrogenating yields a mixture of ethylnortricyclene and ethylnorbornane.
- [0052] Embodiment 15 is the method of any one of embodiments 3-14, wherein the product mixture is substantially free of ethylidene norbornene.
- [0053] Embodiment 16 is the method of any one of embodiments 1-15, wherein contacting ethylidene norbornene with an isomerization catalyst occurs substantially solvent free.
- [0054] Embodiment 17 is the method of any one of embodiments 1-16, wherein contacting ethylidene norbornene with an isomerization catalyst occurs at a temperature in a range of about 35°C to about 400°C, or about 100°C to about 300°C, or about 125°C to about 225°C, or about 150°C to about 200°C, or about 180°C.
- [0055] Embodiment 18 is the method of any one of embodiments 1-17, wherein the isomerization catalyst comprises one or more of activated acidic alumina, a zeolite, titania, and zirconia.
- [0056] Embodiment 19 is the method of any one of embodiments 2-18, wherein the metathesis catalyst is a ring-opening metathesis polymerization catalyst.
- [0057] Embodiment 20 is the method of any one of embodiments 2-19, wherein the metathesis catalyst comprises one or more of a Grubbs Catalyst®, a Hoveyda-Grubbs catalyst®, a Schrock type catalyst, a Ziegler-Natta catalyst, and a ROMP catalyst comprising one or more cyclic(alkyl)(amino) carbene ligands.

[0058] Embodiment 21 is the method of any one of embodiments 2-20, wherein the metathesis catalyst comprises a first generation Grubbs Catalyst®, a second generation Grubbs Catalyst®, a first generation Hoveyda-Grubbs catalyst® a second generation Hoveyda-Grubbs catalyst®, or a third generation Grubbs catalyst®.

[0059] Embodiment 22 is the method of any one of embodiments 2-21, wherein the metathesis catalyst is a second generation Hoveyda-Grubbs Catalyst®.

[0060] Embodiment 23 is a method of synthesizing ethylnorbornene, the method comprising:

contacting ethylidene norbornene with an isomerization catalyst to yield a first mixture comprising ethylidene norbornene and vinylnorbornene;

separating vinylnorbornene from ethylidene norbornene of the first mixture to yield a second mixture comprising vinylnorbornene;

separating the vinylnorbornene from the second mixture to yield a product mixture comprising vinylnorbornene; and

hydrogenating the vinylnorbornene to yield ethylnorbornene.

[0061] Although this disclosure contains many specific embodiment details, these should not be construed as limitations on the scope of the subject matter or on the scope of what may be claimed, but rather as descriptions of features that may be specific to particular embodiments. Certain features that are described in this disclosure in the context of separate embodiments can also be implemented, in combination, in a single embodiment. Conversely, various features that are described in the context of a single embodiment can also be implemented in multiple embodiments, separately, or in any suitable sub-combination. Moreover, although previously described features may be described as acting in certain combinations and even initially claimed as such, one or more features from a claimed combination can, in some cases, be excised from the combination, and the claimed combination may be directed to a sub-combination or variation of a sub-combination.

[0062] Particular embodiments of the subject matter have been described. Other embodiments, alterations, and permutations of the described embodiments are within the scope of the following claims as will be apparent to those skilled in the art. While operations are depicted in the drawings or claims in a particular order, this should not be understood as requiring that such operations be performed in the particular order shown or in sequential order, or that all illustrated operations be performed (some operations may be considered optional), to achieve desirable results.

[0063] Accordingly, the previously described example embodiments do not define or constrain this disclosure. Other changes, substitutions, and alterations are also possible without departing from the spirit and scope of this disclosure.

WHAT IS CLAIMED IS:

1. A method of synthesizing vinylnorbornene, the method comprising:
contacting ethylidene norbornene with an isomerization catalyst to yield a first mixture comprising ethylidene norbornene and vinylnorbornene; and
separating vinylnorbornene from ethylidene norbornene of the first mixture to yield a second mixture, wherein the second mixture comprises at least about 90 mol% vinylnorbornene.
2. The method of claim 1, wherein separating vinylnorbornene from ethylidene norbornene of the first mixture comprises contacting the first mixture with a metathesis catalyst to yield the second mixture.
3. The method of claim 1 or 2, further comprising separating the vinylnorbornene from the second mixture to yield a product mixture comprising vinylnorbornene.
4. The method of claim 3, wherein separating the vinylnorbornene from the second mixture comprises distilling the second mixture.
5. The method of claim 4, wherein distilling the second mixture occurs at a temperature in a range of about 50°C to about 200°C, or about 75°C to about 175°C, or about 125°C to about 150°C.
6. The method of claim 4 or 5, wherein distilling the second mixture occurs at ambient pressure.
7. The method of any one of claims 1-6, further comprising hydrogenating the vinylnorbornene to yield ethylnorbornene.
8. The method of claim 7, wherein the hydrogenating comprises contacting the vinylnorbornene with a catalyst and H₂.
9. The method of claim 8, wherein the catalyst comprises a metal, a metal oxide, or both.
10. The method of claim 8 or 9, wherein the catalyst comprises NiO, Ni, Pd/C, Ru, Ru/C, Ru₂O₃, Ru/alumina, PdO, PtO₂, dichlorotris(triphenylphosphine)ruthenium(II), or cyclooctadiene rhodium(I) chloride.
11. The method of claim 8, wherein the catalyst is a homogeneous catalyst.

12. The method of any one of claims 7-11, wherein the hydrogenating occurs at a temperature of less than about 90°C, or in a range of about 50°C to about 85°C, or about 65°C to about 85°C.
13. The method of any one of claims 7-12, wherein the hydrogenating comprises H₂ at a pressure of about 25 psi to about 250 psi, or about 100 psi to about 200 psi, or about 150 psi.
14. The method of any one of claims 7-13, wherein the hydrogenating yields a mixture of ethylnortricyclene and ethylnorbornene.
15. The method of any one of claims 3-14, wherein the product mixture is substantially free of ethylidene norbornene.
16. The method of any one of claims 1-15, wherein contacting ethylidene norbornene with the isomerization catalyst is substantially free of a solvent.
17. The method of any one of claims 1-16, wherein contacting ethylidene norbornene with the isomerization catalyst occurs at a temperature in a range of about 35°C to about 400°C, or about 100°C to about 300°C, or about 125°C to about 225°C, or about 150°C to about 200°C, or about 180°C.
18. The method of any one of claims 1-17, wherein the isomerization catalyst comprises one or more of activated acidic alumina, a zeolite, titania, and zirconia.
19. The method of any one of claims 2-18, wherein the metathesis catalyst is a ring-opening metathesis polymerization catalyst.
20. The method of any one of claims 2-19, wherein the metathesis catalyst comprises one or more of a Grubbs Catalyst®, a Hoveyda-Grubbs catalyst®, a Schrock type catalyst, a Ziegler-Natta catalyst, and a ROMP catalyst comprising one or more cyclic(alkyl)(amino) carbene ligands.
21. The method of any one of claims 2-20, wherein the metathesis catalyst comprises a first generation Grubbs Catalyst®, a second generation Grubbs Catalyst®, a first generation Hoveyda-Grubbs catalyst®, a second generation Hoveyda-Grubbs catalyst®, or a third generation Grubbs catalyst®.
22. The method of any one of claims 2-21, wherein the metathesis catalyst is a second generation Hoveyda-Grubbs Catalyst®.

23. A method of synthesizing ethylnortricyclene, the method comprising:
- contacting ethylidene norbornene with an isomerization catalyst to yield a first mixture comprising ethylidene norbornene and vinylnortricyclene;
 - separating vinylnortricyclene from ethylidene norbornene of the first mixture to yield a second mixture comprising vinylnortricyclene;
 - separating the vinylnortricyclene from the second mixture to yield a product mixture comprising vinylnortricyclene; and
 - hydrogenating the vinylnortricyclene to yield ethylnortricyclene.