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The facile preparation of alkenyl metathesis synthons

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Dedicated to Professor Robert H. Grubbs on the occasion of his receiving the Tetrahedron Prize for Creativity in Organic Chemistry

Abstract—We report synthetic methodology allowing the preparation of any length alkenyl halide from inexpensive starting reagents. Standard organic transformations were used to prepare straight chain α-olefin halides in excellent overall yields with no detectable olefin isomerization and full recovery of any unreacted starting material. Reported transformations can be used for the selective incorporation of pure α-olefin metathesis sites in highly functionalized molecules.
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1. Introduction

Olefin metathesis has emerged as one of the primary methods for mild carbon–carbon bond formation in organic synthesis, having been widely used across many areas of chemical research. Functional group tolerant ruthenium based catalysts permit the metathesis of highly functionalized compounds that were previously incompatible with traditional catalysts.[1] The development of these stable and reactive catalysts, such as Grubbs' second-generation complex, has expanded metathesis' utility in polymer chemistry[2,3] and more recently in small molecule synthesis.[4–8] Difficult cross-metathesis and ring-closing metathesis reactions can now be accomplished allowing access to large ring systems[9] and functionalized polymer architectures.[10] The application of efficient and mild transformations such as ring closing metathesis (RCM),[11] ring opening metathesis (ROM),[12] and cross-metathesis (CM) has led to pervasive use of olefin metathesis in small molecule and polymer chemistry.[13]

In general, RCM is valuable for selective and efficient ring closures of large functionalized natural products and supramolecularly organized substrates.[14] Application of ROM in combination with CM effectively produces complex ring-opened cross-metathesis products from the coupling of cyclic and linear olefins; this method has been used to connect large molecules and is readily applied in total synthesis.[15] In addition, advances in CM and the understanding of olefin reactivity have stimulated the development of complex synthetic schemes where two or more olefins can be reacted regio- and stereoselectively forming only the target olefin in excellent yields.[16] Acyclic diene metathesis (ADMET), a special form of CM yielding polymers, has been used in materials synthesis and industrial polymer modeling.[2] This rapid rise in olefin metathesis popularity, utility, and catalyst improvement has generated the need for inexpensive, high yielding α-olefin constructs and the means of incorporating metathesis sites into various complex architectures.

We now report three facile and inexpensive synthetic routes to a family of pure α-alkenyl halide metathesis synthons possessing exact methylene run lengths. These synthetic procedures and routine purification methods afford high yields of olefins with no detectable double bond isomerization. The mild transformations reported can also be used to place olefins in highly functionalized molecules without the need for expensive starting materials.

2. Results and discussion

Metathesis ideology has fueled the development of next generation catalyst systems for the production of specific, highly functionalized target molecules for medical and consumer use. Consequently, a large scale, high-yielding α-olefin synthesis is needed to produce molecules for subsequent substitution and metathesis chemistry. Before any metathesis can occur, olefins must be incorporated into substrates where mild and inexpensive techniques would be

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preferred for the creation of target olefins. While well-known literature techniques yield α-olefins directly or transform complex substrates into metathesis active compounds, unwanted side reactions occur leading to low yields.[17,18] This makes recovery of pure starting materials difficult and expensive, while reaction products are sometimes extensively isomerized. These are common problems associated with α-olefin synthesis, and they often lead to structural defects when isomerized olefins are used in metathesis transformations.

Metathesis strategy in small molecule modification typically targets one specific regio- and stereoselective attachment of functionality to produce a high yield of a single molecule. While this facet of synthesis is important, controlling the number of methylene units between olefins is paramount when targeting specific ring size or exact structure. With this in mind, acyclic diene metathesis (ADMET) polymerization of symmetrical α,ω-diene monomers and ROMP of symmetrical cyclic olefins have become the polymerization methods of choice for the preparation of polymers with exact repeat units.

Substrate purity for metathesis reactions is essential, as structural flaws lead to low yielding ring closures, the isolation of the wrong metathesis products, or ill-defined polymer microstructure. Inclusion of internal and external olefins as starting materials in metathesis poses problems as methylene run lengths within product structure will be varied based on extent of olefin isomerization. In the case of small molecule synthesis, variable methylene content in the substrate yields different ring-sizes for RCM or incorrect methylene run lengths for ROM or CM reactions (Scheme 1). The inclusion of isomerized olefins in starting material synthesis creates ill-defined structures leading to numerous olefinic products.

The construction of ADMET monomers and isolation of exact polymer structures begins with the synthesis of pure α-olefins. Errors due to inclusion of isomerized olefins during polymer synthesis become multiplied with high olefin turnover, and ultimately these errors produce random polymer structures and ill-defined methylene run lengths between functional groups. These defects are detrimental for polymer modeling studies and lead to poor material properties relative to polymers obtained from purely α-olefins.[19] We have addressed these problems starting with the inexpensive synthesis of 1-alkenyl bromides, reagents that can be regarded as metathesis synthons in ADMET, cross-metathesis, and RCM chemistry (Scheme 1).

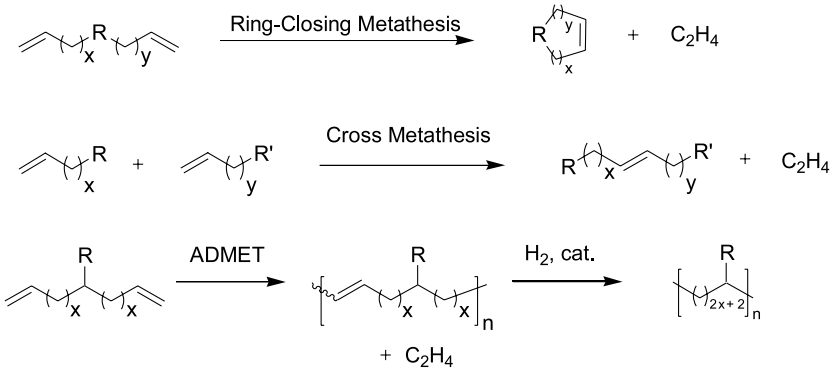
We have devised two routes to these synthons; the preparation of pure α,ω-alkenyl halides was performed either by the reduction of alkenyl esters or through the elimination of HBr from alkyl dibromides. Both routes are described herein, along with a procedure to generate long chain α-alkenyl halide synthons.

2.1. Alkenyl halide metathesis synthons from alkenyl esters

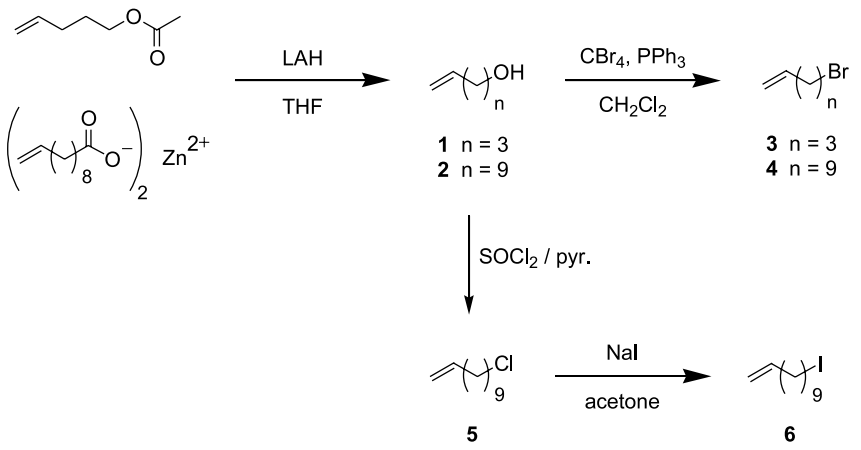
The key to success in generating ADMET, cross-metathesis and RCM dienes is found in locating a source of pure α-alkenyl halide bulk starting materials. Numerous sources of such starting materials exist based on alkenyl esters derived from fatty acids with no isomerization of the pendent olefin. These molecules can be easily reduced to their corresponding alcohols, and literature describing the reduction of various alkenyl esters extends to the 1940s including LAH reactions,[20–23] titanium mediated reductions of esters,[24,25] and polymethylhydrosilane reductions.[26] We have chosen the inexpensive conversion of an α-olefin ester or carboxylate to an alcohol using LAH in THF (Scheme 2). This method was chosen specifically for the reduction of 4-pentenyl ester as the byproduct ethanol could be easily removed via rotary evaporation.

These inexpensive reactions were done on the 100-gram scale in a large flask with sufficient volume for post reaction workup. Upon product isolation, compounds **1** and **2** were characterized via ^{1}H NMR and GC with no detectable olefin isomerization and above 90% purity. Both alkenyl alcohols were clean enough to move onto the next transformation without any further purification.

Conversion of these alkenyl alcohols to corresponding bromides was done using carbon tetrabromide and triphenyl phosphine. This reaction appears to be the most efficient route when considering all reasonable possibilities including the use of phosphorus tribromide,[27] bromine,[28] trifluoro aceticanhydride,[29] and various other conversions that first convert the alcohol to a good leaving group such as a mesylate[30,31] or a silyl ether.[32] The bromination with CBr_4 proceeded quickly and was complete almost as fast as all components could be mixed. The byproduct acid,



Scheme 1. Cross-metathesis, ring closing metathesis and the ADMET reaction.



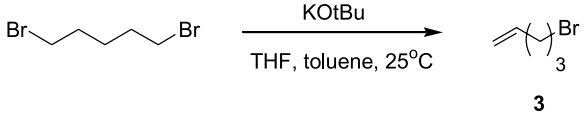
Scheme 2. Alkenyl halide synthesis.

bromoform, does not isomerize the olefin and allows for isolation of clean α-olefin in good yields.

Synthesis of chlorine-functionalized α-olefins has been previously reported and is usually performed neat via addition of $SOCl_2$ to the liquid alcohol.[21–23] We performed this conversion by adding the $SOCl_2$ to a solution of alkenyl alcohol **2** in pyridine acting as a solvent and an acid trap. Upon vacuum distillation, the alkenyl chloride **5** was obtained in good yield. Conversion of the chloride to the alkenyl iodide was performed by a Finkelstein reaction with sodium iodide in acetone.[33]

2.2. Alkenyl halide metathesis synthons via selective dihalide elimination

A method of olefin incorporation within molecules was desired in addition to the production of inexpensive starting reagents for metathesis synthesis. Mild elimination conditions were developed allowing a second method of α-olefin production that could also permit olefin incorporation in functionalized molecules where application of substitution chemistry is unavailable. Literature methods designed to prepare alkenes and alkenyl halides involve the elimination of bromo and dibromo alkanes using hexamethylphophortriamide (HMPT).[17,18] This route is expensive and potentially dangerous due to the highly carcinogenic compound HMPT. Harsh conditions and the highly reactive HMPT lead to a myriad of byproducts that interfere with purification and further, the high temperatures needed for this conversion (150 °C) can result in olefin isomerization in addition to halide elimination. One other disadvantage to this elimination chemistry is the inability to recover unreacted starting material from the complex reaction mixture. Recently, a potassium butoxide elimination has been reported affording alkenyl halides in good yield.[34] A milder, higher yielding room temperature route is presented in Scheme 3.



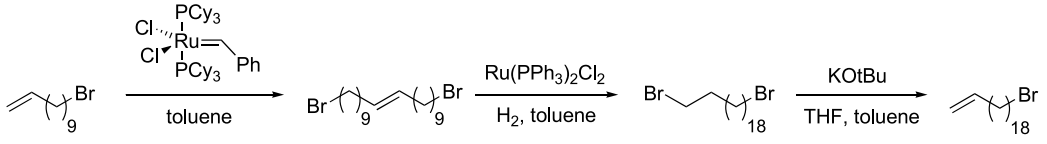
Scheme 3. A mild elimination route towards the synthesis of alkenyl bromide metathesis synthons.

Simple KO*t*Bu driven elimination in a THF/toluene solvent mixture produces the target molecules in ~65% yield. This elimination reaction is started at 0 °C and is allowed to warm to room temperature over 1 h. Upon quenching with aqueous acid, the dibromide/alkenyl bromide mixture can be easily purified affording the target molecule. The recovered dibromide can be recycled for further conversion to alkenyl bromide as necessary.

2.3. Synthesis of larger alkenyl bromide metathesis synthons

Up to this point, the incorporation of metathesis sites into target molecules has been limited by commercial availability and expense of alkenyl bromides. This is especially true when considering the preparation of longer chain alkenyl bromides, a problem that has been overcome by exploiting and extending the chemistry described in the previous sections. As an example of this strategy, we synthesized an alkenyl bromide containing 20 carbons, a molecule which is commercially unavailable.

The synthesis of extended alkenyl bromides began with the self-metathesis of **4** with Grubbs' first generation catalyst to afford **7** (Scheme 4). This dibromide was converted to **8** by exhaustive hydrogenation in a Parr bomb with Wilkinson's Rh catalyst under hydrogen pressure. The saturated 20-carbon dibromide **8** was then converted to the target



Scheme 4. The preparation of long chain alkenyl bromide metathesis synthons.

extended chain alkenyl bromide **9** using the same elimination procedure previously described for smaller alkenyl bromides. Pure compound **9** was obtained in good yield after recrystallization and column chromatography, and recovery of the pure starting reagents was accomplished during purification since very few side reactions accompany these mild transformations.

3. Conclusions

Three mild, inexpensive routes have been devised for the production of pure α-olefin containing halides as metathesis synthons. Using these methods, virtually any 1-alkenyl bromide can be made in high yields and devoid of olefin isomerization. Many of the reactions discussed here are either quantitative in nature, or the starting reagent can be easily recovered for further use.

4. Experimental

4.1. General information

All ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ on a Varian Associates Mercury 300 spectrometer. Chemical shifts are given in ppm and referenced to residual $CHCl_3$ at 7.27 ppm (^{1}H) and 77.23 ppm (^{13}C) with 0.03 v/v% TMS as an internal standard. Splitting patterns are designated s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Gas chromatography was performed on a Shimadzu GC-17A chromatograph equipped with a RTX-5 (Restek Corp.) 15 m column and a HP-5 (Hewlett Packard) 25 m column with FID detection. Compounds were examined using mass spectrometry performed by The University of Florida Mass Spectrometry Services and elemental analysis performed by Atlantic Microlabs (Norcross, GA).

4.2. Materials

All starting materials were purchased from Aldrich except for acetic acid 4-pentenyl ester, which was supplied by TCI America. Grubbs' first generation [Ru] catalyst was synthesized as previously described by Grubbs et al.[35] Dry solvents were collected using an Aldrich keg system removing residual water by alumina filtration.

4.3. Synthesis of alkenyl alcohols

4.3.1. 4-Pentene-1-ol (1). Acetic acid pent-4-enyl ester (250 mL, 1.77 mol) was added dropwise over 2 h to a slurry of LAH (23.7 g, 0.625 mol) in diethyl ether (500 mL) at 0 °C. The solution was allowed to warm to room temperature over 1 h while stirring. The reaction was quenched via the sequential addition of 23 mL deionized water (23 mL), 15% (w/v) NaOH (23 mL), and deionized water (69 mL) waiting approximately 5 min between additions. The solution was allowed to stir the mixture became a bright white slurry. Additional ether (~125 mL) was added and the solution was filtered, dried over $MgSO_4$, and concentrated to a colorless oil. Compound **1** was obtained in 85% yield and 97% purity by GC. The ^{1}H NMR spectrum was consistent with the published spectrum.[36]

4.3.2. 10-Undecene-1-ol (2). Zinc undecylenate (250 g, 0.579 mol) was added over 30 min via powder funnel to a stirred slurry of LAH (25.0 g, 0.659 mol) in dry THF (400 mL) in a 5 L round bottom flask at 0 °C. After the addition, the solution was allowed to warm to room temperature over 1 h while stirring. The reaction was quenched via addition of deionized water (25 mL), 15% (w/v) NaOH (25 mL), and more water (75 mL) waiting approximately 15 min between additions. The solution was allowed to stir until cool, and the reaction mix appeared as a white slurry. All precipitate was filtered, and the solution was concentrated to a turbid oil. The crude mixture was dissolved in ether (100%, v/v) and stirred over $MgSO_4$ (15 g) for 45 min. The solution was filtered and concentrated to afford compound **2** as a colorless oil in 87% yield (97% pure by GC). The ^{1}H NMR spectrum was consistent with the published spectrum.[24]

4.4. Synthesis of alkenyl halides from alkenyl alcohols

4.4.1. 5-Bromo-1-pentene (3). A solution of **1** (100 g, 1.16 mol) and carbon tetratbromide (424 g, 1.27 mol) in dichloromethane (500 mL) was prepared in a 2 L flask and cooled to 0 °C. Triphenyl phosphine (333 g, 1.28 mol) was added via powder funnel in portions over 30 min with vigorous stirring. Upon addition of the phosphine, the colorless solution turned a pale brown color and was stirred for an additional 2 h at room temperature. The mixture was concentrated to a brown oil and quickly added to stirring hexane (1 L). The white precipitate was filtered, and the remaining solution was concentrated and fractionally distilled yielding compound **3** as a colorless oil (80%). The ^{1}H NMR spectrum was consistent with the published spectrum.[37]

4.4.2. 11-Bromo-1-undecene (4). Using the procedure outlined for compound **3** (above), bromide **4** was prepared using alcohol **2** (150 g, 0.881 mol), carbon tetrabromide (323 g, 0.976 mol), triphenyl phosphine (255 g, 0.976 mol), and 800 mL of dichloromethane. Fractional distillation yielded compound **4** as a colorless liquid (95%). The ^{1}H NMR spectrum was consistent with the published spectrum.[28]

4.4.3. 11-Chloro-1-undecene (5). In an argon purged 3 L round bottom flask, distilled thionyl chloride (259 g, 2.17 mol) was added dropwise over 1 h via cannula into a solution of **2** (200 g, 1.28 mol) in pyridine (50 mL). Upon compete addition, the reaction was heated to 50 °C for 2 h, cooled, and quenched via the addition of water (300 mL) and diethyl ether (300 mL) letting stir for 1 h. The remaining mixture was extracted, and the organic phase was washed with saturated $NaHCO_3$ (2×150 mL) and distilled water (100 mL). The solution was dried over $MgSO_4$, concentrated, and vacuum distilled to a colorless oil **5** (70%). The ^{1}H NMR spectrum was consistent with the published spectrum.[38]

4.4.4. 11-Iodo-1-undecene (6). Sodium iodide (40.7 g, 0.271 mol) was added to distilled **5** (30.6 g, 0.162 mol) in

acetone (150 mL) and allowed to reflux for 3 days. The reaction mixture was then cooled and flooded with ether (300 mL). The precipitate was filtered and the ether solution was washed with water (2×100 mL). The organic layer was extracted, dried with $MgSO_4$, filtered, and concentrated to a colorless oil **6** (89%). The ^{1}H NMR spectrum was consistent with the published spectrum.[39]

4.5. Synthesis of alkenyl bromides from dibromides

4.5.1. 5-Bromo-1-pentene (3). In a 1 L round bottom flask 1,5-dibromopentane (100 g, 0.434 mol) was dissolved in 450 mL of a 1:1 THF/toluene solution to favor the single eliminated product. The flask was cooled to 0 °C followed by the addition of solid KO*t*Bu (73.0 g, 0.651 mol) over 30 min. After addition, the reaction was quenched using 1 M HCl (300 mL) and the organic layer was extracted, washed with saturated Na_2CO_3 (100 mL), and dried over magnesium sulfate. The solution was concentrated and distilled yielding 44 g of compound **3** (69%). The ^{1}H NMR spectrum was consistent with the published spectrum.[37]

4.5.2. 1,20-Dibromo-eicos-10-ene (7). In an argon filled glove box, compound **4** (100 g, 429 mmol) was added to a 500 mL round bottom flask followed by Grubbs' catalyst (706 mg, 0.885 mmol, 500:1). The flask was heated at 35 °C for 24 h under a constant stream of argon. After 1 day, the flask was placed under vacuum (10 Torr) for an additional 48 h, cooled, and quenched with ethyl vinyl ether (5 mL). The crude reaction mixture was dissolved in toluene (200 mL) and precipitated into methanol (1000%, v/v) over the course of 30 min. The product was filtered as a white crystalline solid and washed with excess methanol yielding 75 g (80%). The following spectral properties were observed: ^{1}H NMR ($CDCl_3$): δ (ppm) 1.20–1.50 (br, 24H), 1.88 (q, 4H, $J_1=7.0$ Hz, $J_2=7.0$ Hz, CH_2CH_2Br), 2.01 (m, 4H, allylic CH_2), 3.42 (t, 4H, $J=6.7$ Hz, CH_2Br), 5.40 (m, 2H, olefin); ^{13}C NMR ($CDCl_3$): δ (ppm) 28.4, 29.3, 29.7, 29.8, 32.8, 33.1, 34.4, 130.3; EI/HRMS: $[M]^+$ calcd for $C_{20}H_{38}Br_2$: 438.1322, found: 438.1312.

4.5.3. 1,20-Dibromo-eicosane (8). In a 125 mL Parr bomb glass sleeve, compound **7** (35 g, 80 mmol) was dissolved in a minimal amount of toluene (~80 mL). Wilkinson's Rh hydrogenation catalyst (100 mg, 0.104 mmol) was added, and the bomb was charged with 800 psi of hydrogen. The reaction was allowed to proceed for 24 h at 50 °C. Additional toluene (200 mL) was added, and upon cooling to 0 °C, the product **8** crystallized out of solution and was collected by filtration. The filtrate was concentrated (~50%), and the product was allowed to crystallize again. Upon isolation of the product from the second crystallization, both portions were combined and washed with cold toluene. Yield: 30 g (86%). The following spectral properties were observed: ^{1}H NMR ($CDCl_3$): δ (ppm) 1.28 (br, 28H), 1.42 (m, 4H, $J=6.7$ Hz), 1.88 (q, 4H, $J_1=6.7$ Hz, $J_2=7.2$ Hz, CH_2CH_2Br), 3.42 (t, 4H, $J=6.9$ Hz, CH_2Br); ^{13}C NMR ($CDCl_3$): δ (ppm) 28.4, 29.7, 29.8, 30.0, 33.1, 34.4; EI/HRMS: $[M]^+$ calcd for $C_{20}H_{40}Br_2$: 440.1478, found: 440.1616.

4.5.4. 20-Bromo-eicos-1-ene (9). In a 1 L round bottom flask compound **8** (50 g, 113 mmol) was dissolved in 2:1 THF/toluene mixture producing a 1 M solution. The mixture was cooled using an ice water bath, and potassium *tert*-butoxide (19.0 g, 170 mmol) was added in 2 g portions over 30 min. After addition, the reaction turned cloudy and was allowed to stir at 0 °C for 1 h. The reaction was quenched using water (100 mL) followed by 1 M HCl (100 mL). The organic layer was extracted and washed with 1 M HCl (50 mL), saturated Na_2CO_3 (50 mL), and 50 mL of water followed by drying with magnesium sulfate. The solution was concentrated yielding 38 g of crude material. Compound **9** was purified by room temperature recrystallization from 1-butanol (5 w/v%) followed by column chromatography using hexane. Compound **9** was collected as white solid. Yield: 24 g (60%). The following spectral properties were observed: ^{1}H NMR ($CDCl_3$): δ (ppm) 1.20–1.50 (br, 30H), 1.88 (q, 2H, $J=7.2$ Hz, CH_2CH_2Br), 2.01 (q, 2H, allylic CH_2), 3.42 (t, 2H, $J=6.9$ Hz, CH_2Br), 5.09 (m, 2H, $RHC{=}CH_2$), 5.76 (m, 1H, $RHC{=}CH_2$); ^{13}C NMR ($CDCl_3$): δ (ppm) 28.4, 29.3, 29.7, 29.8, 32.8, 33.1, 34.4, 114.3, 139.4; EI/HRMS: $[M]^+$ calcd for $C_{20}H_{39}Br$: 358.2235, found: 358.2246.

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