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Note

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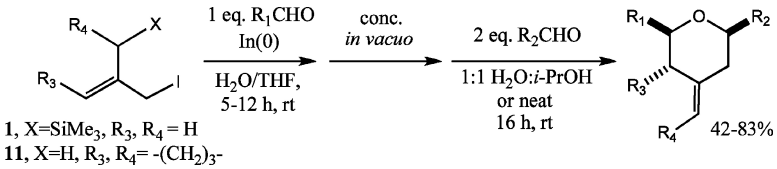

1, X=SiMe$_3$, R$_3$, R$_4$ = H
11, X=H, R$_3$, R$_4$= -(CH$_2$)$_3$-

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An Environmentally Benign Synthesis of *cis*-2,6-Disubstituted Tetrahydropyrans via Indium-Mediated Tandem Allylation/Prins Cyclization Reaction

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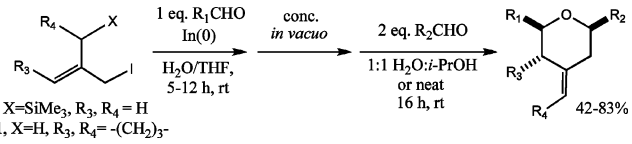

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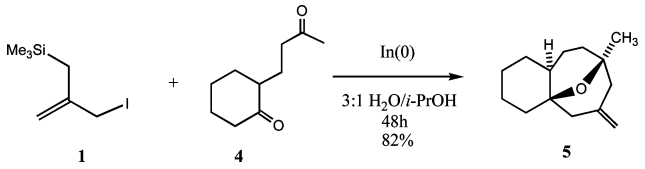
11, X=H, R$_3$, R$_4$= -(CH$_2$)$_3$-

In the presence of indium metal, 3-iodo-2-[(trimethylsilyl)-methyl]propene (**1**) reacts with sequentially added aldehydes to provide *cis*-2,6-disubstituted tetrahydropyrans in good yields. Evidence suggests that InI, formed upon aldehyde (R_1CHO) allylation in aqueous media, acts as a promoter for the silyl-Prins reaction with the second equivalent of added aldehyde (R_2CHO). The preparation of cyclohexenyl-fused pyrans via this one-pot, three-component coupling process is presented, as is a short formal synthesis of (±)-centrolobine.

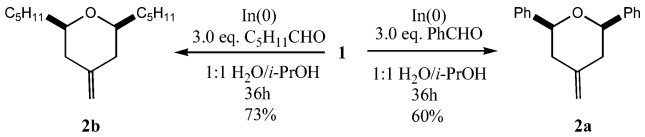
The widespread occurrence of substituted tetrahydropyran moieties in natural products has inspired the development of numerous creative synthetic approaches to this important structural subunit.[1] Although these methods are highly efficient, the typical requirements for strictly anhydrous conditions, strong Lewis acid promoters, low temperatures, and/or halogenated solvents, may be seen as limitations.[2,3] Herein we report an environmentally benign one-pot preparation of 2,6-disubstituted tetrahydropyrans in aqueous media employing indium metal as the sole promoter.

SCHEME 1. An Indium-Mediated [*m* + *n*] Annulation Reaction



1 **4** **5**

SCHEME 2. Indium-Mediated Reactions of 1 with Aldehydes in Aqueous Media



2b **2a**

We have previously reported that combination of equimolar amounts of 3-iodo-2-[(trimethylsilyl)methyl]propene (**1**),[4] dicarbonyl compounds (**4**), and indium metal gives rise to seven- and eight-membered oxa-bridged carbocycles (**5**) in moderate to high yields (Scheme 1).[5] This [*m* + *n*] annulation process takes place in aqueous media at room temperature under an atmosphere of air and requires no externally added Lewis acid promoter. We have proposed that indium-mediated intermolecular allylation of one carbonyl of the substrate is followed by an intramolecular silyl-Prins cyclization reaction promoted by the indium halide salts (or Brønsted acids derived therefrom) formed in the allylation step.

To verify that two monocarbonyl compounds could also participate in this process, we added an excess (3.0 equiv) of benzaldehyde to **1** and indium metal in 1:1 H_2O/*i*-PrOH and stirred the reaction mixture at ambient temperature for 36 h (Scheme 2). 2,6-Diphenyltetrahydropyran **2a** was obtained in 60% yield; repetition of this reaction with 3.0 equiv of hexanal instead gave rise to 2,6-dipentyltetrahydropyran **2b** in 73% yield. In both cases, a single stereoisomer was predominant (>13:1 stereoselectivity by GC−MS analysis of the crude reaction mixture), and ^{1}H and ^{13}C NMR spectra for **2a** were in accord with literature data[6] reported for the *cis* isomer.

Given the efficiency with which symmetrical tetrahydropyrans could be obtained by this process, we next explored the possibility of preparing unsymmetrical tetrahydropyrans by employing two different aldehydes added sequentially during the reaction. Thus, stirring equimolar amounts of **1**, hexanal, and indium metal in 1:1 H_2O/*i*-PrOH at room temperature for 10 h, followed by addition of 2.0 equiv of benzaldehyde and stirring for 24 h, led to the formation of unsymmetrical tetrahydropyran **2c** in 45% yield (Scheme 3), along with symmetrical tetrahydropyran **2b** (10% yield) and homoallylic alcohol **10** (40%). Further analysis of the reaction revealed that hexanal is not completely consumed in its reaction with **1** in the initial allylation step, and the intermediate homoallylic

(1) For a recent review of strategies for the formation of tetrahydropyran rings in the synthesis of natural products, see: (a) Clarke, P.A.; Santos, S. *Eur. J. Org. Chem.* **2006**, *9*, 2045. For examples of 2,6-disubstituted tetrahydropyrans in natural product synthesis, see: (b) Clarke, P. A.; Martin, W. H. C. *Tetrahedron* **2005**, *61*, 5433. (c) Smith, A. B., III; Safonov, I. G. *Org. Lett.* **2002**, *4*, 635. (d) Smith, A. B., III; Safonov, I. G.; Corbett, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 12426.

(2) For recent efforts toward the construction of tetrahydropyran rings, see: (a) Clarke, P. A.; Martin, W. H. C. *Tetrahedron Lett.* **2004**, *45*, 9061. (b) Marko, I. E.; Plancher, J.-M. *Tetrahedron Lett.* **1999**, *40*, 5259. (c) Marko, I. E.; Leroy, B. *Tetrahedron Lett.* **2000**, *41*, 7225. (d) Leroy, B.; Marko, I. E. *J. Org. Chem.* **2002**, *67*, 8744. (e) Dubost, C.; Marko, Bryans, I. E. J. *Tetrahedron Lett.* **2005**, *46*, 4005. (f) Yu, C.-M.; Lee, J.-Y.; So, B.; Hong, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 161. (g) Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309.

(3) For indium-mediated tetrahydropyran and dihydropyran syntheses, see: (a) Viswanathan, G. S.; Yang, J.; Li, C.-J. *Org. Lett.* **1999**, *1*, 993. (b) Yang, J.; Viswanathan, G. S.; Li, C.-J. *Tetrahedron Lett.* **1999**, *40*, 1627. (c) Zhang, W.-C.; Li, C.-J. *Tetrahedron* **2000**, *56*, 2403. (d) Chan, K.-P.; Loh, T.-P. *Org. Lett.* **2005**, *7*, 4491. (e) Loh, T.-P.; Yang, J.-Y.; Feng, L.-C.; Zhou, Y. *Tetrahedron Lett.* **2002**, *43*, 7193. (f) Chan, K.-P.; Loh, T.-P *Tetrahedron Lett.* **2004**, *45*, 8387. (g) Dobbs, A. P.; Martinovic, S. *Tetrahedron Lett.* **2002**, *43*, 7055.

(4) Compound **1** was prepared (MsCl, Et_3N, THF; NaI, acetone) from the corresponding allylic alcohol: Trost, B. M.; Chan, D. M. T.; Nanninga, N. *Org. Synth.* **1984**, *62*, 58.

(5) Allatabakhsh, A.; Pham, M.; Minehan, T. G. *Heterocycles* **2007**, *72*, 115.

(6) For the spectral data of **2a**, see ref 3e.

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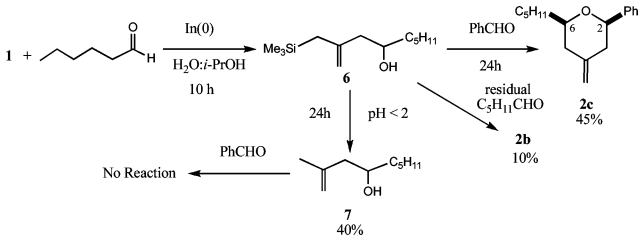
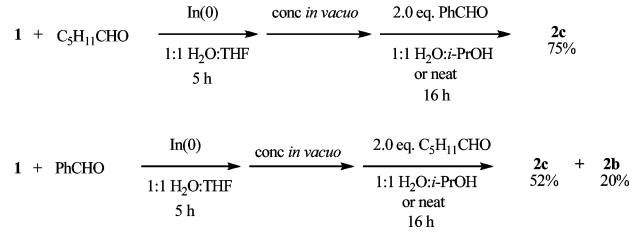
SCHEME 3. Initial Attempts at Preparation of Unsymmetrical Tetrahydropyrans



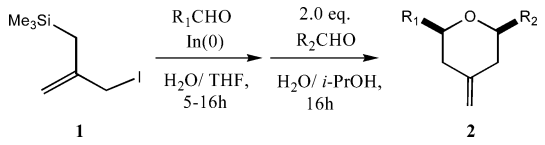
SCHEME 4. Solvent Effect in the Preparation of Unsymmetrical Tetrahydropyrans



alcohol **6** begins to react with residual hexanal to form **2b** even before benzaldehyde is added. Furthermore, since the acidity of the medium increases as allylation proceeds (to pH ~2),[7] protodesilylation of the intermediate homoallylic alcohol **6** becomes a major side reaction over extended reaction times.[8] The resulting alcohol **7** is unreactive toward benzaldehyde under these conditions.

To address these problems, the reaction solvent composition was adjusted. Equimolar amounts of **1**, hexanal, and indium metal were combined in 1:1 H_2O/THF and stirred at room temperature. Complete consumption of the starting materials by TLC analysis was observed within 5 h, and no evidence of **2b** formation could be detected by GC analysis. However, when 2.0 equiv of benzaldehyde was added and the mixture was stirred at room temperature for 16 h, unsymmetrical tetrahydropyran **2c**[3e] was obtained in only 8% yield, with the vast majority of the reaction mixture consisting of homoallylic alcohol **6**, along with some minor amounts (<10%) of **7**. Under the assumption that the Lewis basic solvent THF inhibits the acid-promoted Prins reaction, we subsequently altered the procedure by briefly concentrating the allylation reaction in vacuo (to remove THF) just prior to the addition of benzaldehyde (dissolved in 1:1 H_2O/*i*-PrOH); after stirring the resulting 2 M solution at room temperature for 16 h, a dramatically improved yield of **2c** (75%) was obtained, and only minimal amounts of **7** (<5%) were recovered from the reaction mixture (Scheme 4). It was subsequently discovered that similarly high yields of **2c** (70−80%) could be obtained when the Prins step was performed in the absence of solvent by simply stirring the concentrated allylation reaction mixture with 2 equiv of benzaldehyde overnight. Interestingly, utilizing the same procedures but employing stoichiometric benzaldehyde for the allylation step and 2.0 equiv of hexanal for the Prins reaction resulted in only a 52% yield of **2c**, along with significant amounts (~15−20%) of **2b** (vide infra). GC−MS analysis of all crude reaction mixtures indicated product formation with >15:1 stereoselectivity, and the *cis* stereochemistry of major product **2c** was confirmed by a two-dimensional NMR (NOESY) experiment, in which strong cross-peaks between the axial protons at C2 and C6 were observed (see Supporting Information).

TABLE 1. Scope of Indium-Mediated *cis*-2,6-Tetrahydropyran Synthesis[a]



entry	R_1	R_2	**2**	% yield of **2**[b]
1	Ph	Ph	**a**	76
2	C_5H_{11}	C_5H_{11}	**b**	83
3	C_5H_{11}	Ph	**c**	75
4	C_5H_{11}	4-Cl−Ph	**d**	68
5	*i*-Pr	Ph	**e**	79
6	*i*-Pr	4-Cl−Ph	**f**	65
7	*i*-Pr	C_5H_{11}	**g**	68
8	Ph	4-Cl−Ph	**h**	60[c]
9	$PhCH_2OCH_2$[d]	Ph	**i**	55[c]
10	4-Cl−Ph	4-OMe−Ph	**j**	75
11	Ph	(*E*)-PhCHCH	**k**	65
12	(*E*)-C_5H_{11}CHCH	C_5H_{11}	**l**	60[c]
13	(*Z*)-DPSOCH$_2$CHCH[f]	4-OMe−Ph	**m**	70[e]
14	4-DPSO−$C_6H_4(CH_2)_3$[d,f]	4-OMe−Ph	**n**	50[c,g]

[a] Reaction conditions: **1** + R_1CHO in 1:1 H_2O/THF (1M), 5−12 h; concentration in vacuo, addition of 2.0 equiv of R_2CHO in 1:1 H_2O/*i*-PrOH (2 M), 16 h. [b] Yields refer to products isolated after silica gel chromatography. [c] Lower isolated yields due to formation of symmetrical tetrahydropyran byproducts and/or protodesilylation of the intermediate homoallylic alcohol (see text). [d] Allylation required 24 h stirring at room temperature. [e] Product isolated as a 3:1 mixture of *Z*:*E* olefin isomers. [f] DPS = *tert*-butyldiphenylsilyl. [g] Prins reaction performed in the absence of solvent.

We evaluated the scope of this process by employing a variety of alkyl, aryl, and α,β-unsaturated aldehydes in both the allylation and Prins cyclization steps. As shown in Table 1, diverse *cis*-2,6-disubstituted tetrahydropyrans can be prepared by this method. The two-step, one-pot procedure provides superior yields (compared to using 1:1 H_2O/*i*-PrOH as solvent alone, vide supra) even for the preparation of the symmetrical tetrahydropyrans **2a** and **2b** (entries 1 and 2). It is also noteworthy that acid-labile silyl-protecting groups survive the coupling process (entries 13 and 14,[16] DPS = *tert*-butyldiphe-

(7) Assessed by a simple litmus paper test.

(8) As much as 50% of desilylated homoallylic alcohol was isolated from the reaction mixtures in some cases.

(9) For a discussion on erosion of enantioselectivity and side-chain exchange via the oxonium-Cope rearrangement in Prins reactions, see: (a) Cheng-Hsia, A. L.; Loh, T.-P. *Tetrahedron Lett.* **2006**, *47*, 1641. (b) Crosby, S. R.; Harding, J. R.; King, C. D.; Parker, G. D.; Willis, C. L. *Org. Lett.* **2002**, *4*, 577. (c) Marumoto, S.; Jaber, J. J.; Vitale, J. P.; Rychnovsky, S. D. *Org. Lett.* **2002**, *4*, 3919.

(10) Chan et al. have presented evidence that the intermediate in aqueous indium-mediated allylation reactions is allylindium(I): Chan, T. H.; Yang, T. *J. Am. Chem. Soc.* **1999**, *121*, 3228.

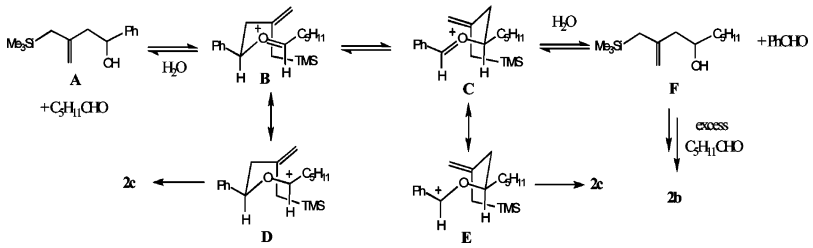
(11) Prepared from commercially available 3-(trimethylsilyl)allyl alcohol (Aldrich) by mesylation (MsCl, Et_3N, CH_2Cl_2, 0 °C) followed by iodide displacement (NaI, acetone, rt, 24 h).

(12) Spectroscopic data (^{1}H, ^{13}C NMR) for **9** matched those reported by Hinkle for the same compound with *syn*-2,6-stereochemistry: (a) Lian, Y.; Hinkle, R. J. *J. Org. Chem.* **2006**, *71*, 7071. Although Li reports the use of *E*-vinylsilanes for the synthesis of dihydropyrans (ref 3a), Brimble reports that the *Z*-configuration of the vinylsilane is crucial for the formation of dihydropyrans: (b) Meilert, K.; Brimble, M. A. *Org. Biolom. Chem.* **2006**, *4*, 2184.

(13) For the preparation of **10**, see: (a) Majetich, G.; Song, J.-S.; Ringold, C.; Nemeth, G. A.; Newton, M. G. *J. Org. Chem.* **1991**, *56*, 3973. (b) Carlson, R. M. *Tetrahedron Lett.* **1978**, *19*, 111.

(14) For an alternative preparation of cyclohexenyl-fused pyrans, see: Loh, T.-P.; Feng, L.-C.; Yang, J.-Y. *Synthesis* **2002**, *7*, 937.

SCHEME 5. Oxonium-Cope Rearrangement Gives Rise to the Symmetrical Tetrahydropyran Byproduct

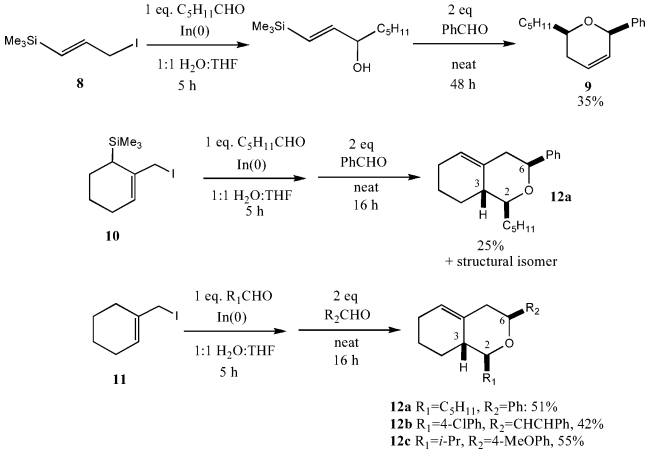


nylsilyl). Reactions requiring longer times for the initial allylation step (entries 9 and 14) resulted in lower overall yields due to partial homoallylic alcohol desilylation (of the trimethylsilyl group) and/or formation of the symmetrical tetrahydropyran byproduct.

Moderate yields were also encountered in the preparation of substrates **2h** and **2l** (entries 8 and 12, respectively), as was the case for preparation of **2c** when benzaldehyde was used for allylation and hexanal for Prins cyclization. These results may be rationalized by noting that the second added aldehyde in each case gives rise to a less stable oxocarbenium ion intermediate (resonance structures **B** and **D**, Scheme 5) than would be obtained from the first added aldehyde; as a result, an alternative reaction pathway involving a [3,3]-sigmatropic oxonium-Cope rearrangement may take place instead of Prins cyclization, leading to a more stable oxocarbenium ion (resonance structures **C** and **E**, Scheme 5).[9] Hydrolysis of ion **C**/**E** to the corresponding aldehyde and homoallylic alcohol (**F**) could then give rise to symmetrical tetrahydropyran byproducts due to reaction of **F** with the excess of second aldehyde present in the reaction medium. As described above in the preparation of **2c** (Scheme 4), this problem can largely be avoided by judicious choice in the order of aldehyde addition (note that the reverse process, ions **C**/**E** → **B**/**D**, should be less favorable).

Several further observations were made in an attempt to elucidate the identity of the promoter of the Prins cyclization process. In the synthesis of **2c**, upon completion of allylindium addition to hexanal, dark burgundy salts are evident in the reaction mixture, perhaps indicating the presence of indium(I) iodide.[10] Concentration of the reaction mixture and addition of benzaldehyde in 1:1 H_2O/*i*-PrOH to make a 2 M solution resulted in a milky-white aqueous suspension (containing dark granules) at pH ∼2. Addition of 0.5 equiv of sodium acetate as a buffer (→ pH 4) at this point completely inhibits the Prins cyclization reaction. Addition of 1 equiv of iodine instead (to presumably oxidize InI to InI_3) and stirring at room temperature for 24 h produced **2c** in low yields (30%). To further probe the identity of the acid (Brønsted or Lewis) promoting the Prins process, isolated homoallylic alcohol **6** (obtained after aqueous extraction, drying, and evaporation of the allylation reaction mixture) was subjected to Prins cyclization with 2 equiv of benzaldehyde in 1:1 0.1 N HCl/*i*-PrOH or in 1:1 H_2O/*i*-PrOH in the presence of either 1 equiv of $InCl_3$ or 1 equiv of InI. Product **2c** was obtained in all three cases, but superior

SCHEME 6. Allylation/Cyclization Reactions of Allyl Iodides 8, 10, and 11



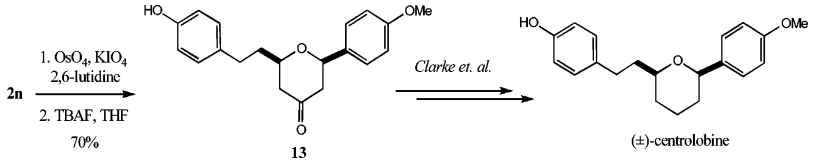
conversions (∼65%) were noted for the reaction promoted by finely ground InI versus that promoted by either $InCl_3$ (20%) or 0.1 N HCl (30%). Surprisingly, simply stirring the isolated homoallylic alcohol **6** together with 2 equiv of benzaldehyde in the absence of either solvent or promoter led to the production of **2c** in approximately 25% yield. Taken together, these data suggest an important role for InI in the Prins cyclization process, along with the unexpected finding that InI is a superior promoter in comparison to $InCl_3$.

With these data in hand, we explored the use of alternative allyl iodides in our one-pot allylation/Prins cyclization procedure. Not surprisingly, combining 1-iodo-3-trimethylsilyl-2-propene **8**[11] with hexanal and benzaldehyde according to our established protocol (with 48 h stirring for the Prins step) furnished dihydropyran **9**[12] in only 35% yield; the intermediate homoallylic alcohol was also recovered in approximately 60% yield (Scheme 6). This result can be rationalized by the requirement for formation of a less stable secondary β-silyl cation during the Prins cyclization step for this substrate. Unexpectedly, however, reaction of iodide **10**[13] with 1 equiv each of indium metal and hexanal in 1:1 H_2O/THF, followed by concentration and addition of excess benzaldehyde, led to a 1:1 mixture of cyclohexenyl-fused pyran **12a**[14] and an unidentified structural isomer in a disappointing 50% overall yield. All attempts to improve the yield of the desired product failed, and by analyzing the structure of the byproduct of this reaction by NMR spectroscopy, we hypothesized that migration of silicon was occurring during the process. As a result, we instead exposed 1-(iodomethyl)cyclohex-1-ene **11**[15] to our allylation/Prins cyclization protocol with a variety of aldehydes. Gratifyingly, when the Prins cyclization step was performed in the absence of solvent, pyrans **12a**−**c** were obtained in moderate yields with a single stereoisomer in excess (>15:1 for **12a**, 10:1 for **12b**, and 13:1 for **12c**). The 11.6 Hz coupling constant of

(15) Compound **11** was prepared from commercially available methyl cyclohexenecarboxylate (Aldrich) by reduction (2.5 equiv of DIBAL-H, THF, −78 °C), mesylation (MsCl, Et_3N, THF), and iodide displacement (NaI, acetone, rt, 24 h).

(16) Aldehyde prepared from commercially available 4-hydroxybenzaldehyde by silylation (TBDPS-Cl, imidazole, DMF, 24 h, rt), Horner−Emmons reaction (triethylphosphonoacetate, NaH, THF), reduction (DIBAL-H, THF, −78 °C), olefin hydrogenation (H_2, 10% Pd−C, rt, 24 h), and oxidation (oxalyl chloride, DMSO, Et_3N, CH_2Cl_2).

SCHEME 7. A Short Formal Synthesis of (±)-Centrolobine



the C2 proton in each product, in addition to the C2 proton−C6 proton cross-peaks in the NOESY spectrum of **12a** (see Supporting Information), confirmed the relative stereochemistry of the major diastereomers as 2,3-*anti*, 2,6-*syn*.

Finally, we realized that product **2n** (Table 1) might serve as an intermediate in a formal synthesis of the natural product centrolobine.[17] Oxidative cleavage of the alkene of **2n** under Jin's conditions,[18] followed by silyl ether deprotection, furnished ketone **13**,[19] a compound that has been converted to racemic centrolobine in quantitative yield by Clarke et al.[20] (Scheme 7).

In summary, we have demonstrated an efficient one-pot synthesis of *cis*-2,6-disubstituted tetrahydropyrans from substituted allyl iodides using indium metal as the sole promoter. This environmentally benign protocol takes place in aqueous media under conditions that tolerate acid-sensitive alcohol protecting groups. Further experiments to extend the scope and delineate the mechanism of this process are underway and will be reported in due course.

Experimental Section

General Procedure for the Synthesis of 2a−n, 12a−c. To a 1 M solution of 3-iodo-2-[(trimethylsilyl)methyl]propene (**1**) in 1:1 THF/H_2O were added R_1CHO (1 equiv) and indium metal (1 equiv). The reaction mixture (wrapped in aluminum foil for protection from light) was stirred at room temperature for 5−12 h. When TLC showed complete disappearance of the starting material, R_2CHO (0.1 equiv) was added and the reaction mixture was concentrated in vacuo on a rotary evaporator. Further R_2CHO (2 equiv) was added, either with 1:1 H_2O/*i*-PrOH (to make a 2 M solution) as solvent or in the complete absence of solvent, and the mixture was stirred at room temperature for 16 h with protection from light. The reaction was then diluted with ether (20 mL) and washed with 1 N HCl (2 × 20 mL). The combined aqueous phases were back-extracted with ether (1 × 50 mL). The combined organic extracts were then dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (silica gel, hexane/Et_2O = 99:1 to 95:5).

(±)-4-Methylene-2-pentyl-6-phenyltetrahydro-2*H*-pyran (2c). Following the general procedure, starting materials **1** (114 mg, 0.44 mmol), hexanal (44 mg, 0.44 mmol), and benzaldehyde (94 mg, 0.88 mmol) were combined to provide **2c** as a colorless oil (81 mg, 0.33 mmol, 75%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.37 (m, 5H), 4.81 (m, 2H), 4.35 (dd, J = 1.6, 10.8 Hz, 1H), 3.45 (m, 1H), 2.50 (d, J = 13.2 Hz, 1H), 2.32 (d, J = 13.2 Hz, 1H), 2.24 (t, J = 12.8 Hz, 1H), 2.06 (t, J = 11.6 Hz, 1H), 1.71−1.32 (m, 7H), 0.92 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 142.8, 128.3, 127.3, 125.8, 108.6, 80.1, 78.8, 42.9, 40.6, 36.3, 31.9, 25.1, 22.6, 14.1; GC−MS *m*/*z* 244 (M^+).

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Supporting Information Available: Detailed experimental procedures, spectroscopic data, and ^{1}H NMR spectra for all compounds in Table 1 and Schemes 6 and 7, as well as NOESY spectra for compounds **2c** and **12a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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