Iodine/AcCl-catalyzed Prins-Ritter reaction: Synthesis of 4-amido tetrahydropyrans

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Homoallylic alcohols, carbonyl compounds and nitriles undergo a smooth tandem Prins-Ritter type cyclization in the presence of iodine/AcCl at room temperature to produce 4-amidotetrahydropryrans in high yields with all cis-selectivity.

Keywords: Tetrahydropyrans, iodine, Prins-Ritter reaction, cyclization, spiro cyclic compounds

The tetrahydropryan ring has attracted significant attention in recent years, as it is a part of the backbone of many natural products\(^1\). It is present widely in many natural products such as phorboxazole A, psymberin and (-)-centrolobine. The 4-amino tetrahydropryan ring system is a core unit in a number of natural products such as ambrucitins VS, glycamino acid and others\(^2\). Because of their prevalence, there are multiple strategies for the construction of these six membered ring systems, including Prins cyclization\(^3\), hetero Diels-Alder reactions\(^4\) and intramolecular nucleophilic reactions\(^5\). Among the many methods available, Prins cyclization offers one of the most versatile methods for the construction of the tetrahydropryan ring.

Iodine was found to be an effective reagent for the cross-coupling of olefins with aldehydes under mild conditions to produce 4-substituted 1,3-dioxane derivatives in excellent yields and in short reaction times with high selectivity\(^6\). 4-Iodopiperidines were prepared in good yields and with high selectivity by means of aza-Prins-cyclization using a catalytic amount of gallium(III) iodide and a stoichiometric amount of iodine under mild reaction conditions\(^7\). Three-component coupling of carbonyl compounds, homoallylic alcohols and nitriles was achieved using 20 mol % of phosphomolybdic acid (PMA) at ambient temperature via the Prins-Ritter sequence to furnish 4-amidotetrahydropryrans in high yields with all cis selectivity. Spirocyclic-4-amidotetrahydropryrans were obtained using cyclic ketones\(^8\). A rapid and efficient BiCl\(_3\) promoted stereoselective synthesis of trans-2,4-disubstituted piperidine derivatives was achieved from N-protected homoallyl amines and epoxides by aza-Prins cyclization\(^9\). Yadav et al. reported the synthesis of 4-azido tetrahydropryrans from aldehydes, homoallylic alcohols and sodium azides in the presence of TFA at room temperature\(^10\). Homoallylic alcohols, carbonyl compounds and nitriles undergo a smooth tandem Prins-Ritter type cyclization in the presence of CeCl\(_3\).7H\(_2\)O/AcCl at ambient temperature to produce 4-amido tetrahydro-
pyrans in high yields with all cis-selectivity. Spirocyclic 4-amido tetrahydropyrans were obtained in the case of cyclic ketones.

A novel synthetic methodology for 2,5-disubstituted tetrahydrofurans having an allenyl group at the 3-position via Prins-type cyclization was developed. Unsaturated enol ethers couples with aldehydes in the presence of TiBr₄ to give 4-bromotetrahydropyrans by Mukaiyama aldol-Prins cyclization. Yadav et al. reported the synthesis of 4-thiocyanotetrahydropyrans from a three-component coupling of aldehydes, homoallylic alcohols and ammonium thiocyanate in the presence of 10 mol % of In(OTf)₃ in refluxing dichloromethane. Tetrahydropyrans were synthesized from allylbromide and carbonyl compounds by one-pot Barbier-Prins cyclization promoted by BPYX/SnX₂ or BBIBMB/SnBr₂ complex (functionalized RTILs) under solvent-free conditions. Epoxides undergo cross-cyclization with homoallylic alcohols in the presence of zirconium tetrachloride under mild conditions to afford the corresponding tetrahydropyran derivatives in excellent yields. 2,4,6-Trisubstituted tetrahydropyrans were formed with high stereoselectivity by a one-pot multi-component Lewis acid catalyzed Prins cyclization. This catalytic method could also be used with α,β-unsaturated aldehydes affording moderate yields of products. A straightforward synthesis of (±)-diospongion A starting from benzaldehyde was described. A Prins cyclization reaction to control the relative configuration of the three stereogenic centers and a Mitsunobu inversion represent the key steps of the approach.

Rovis et al. developed an operationally simple procedure for the highly diastereoselective preparation of 4-acyl-amino-2,6-substituted tetrahydropyrans by a one-pot Sakurai-Prins-Ritter reaction from readily available reagents. Rychnovsky et al. disclosed a new annulation reaction for the synthesis of tetrahydropyran ring via a Mukaiyama-Michael cascade. Aldol reactions of β-ketoesters with aldehydes followed by a tandem Knoevenagel condensation and further reaction with another equivalent of aldehyde and intramolecular Michael addition produces single diastereomer of highly substituted tetrahydropyran-4-ones. Potassium permanganate promoted oxidative cyclization of 1,6-dienes gave cis-2,6-bis-hydroxyalkyl-tetrahydropyrans in good yields.

Recently, molecular iodine has received considerable attention as an inexpensive, non-toxic, readily available catalyst for various organic transformations, affording the corresponding products with high selectivity in excellent yields. The mild Lewis acidity associated with iodine enhanced its usage in organic synthesis to give several organic transformation using stoichiometric levels to catalytic amounts. Owing to advantages associated with this eco-friendly catalyst, molecular iodine has been explored as a powerful catalyst for various organic transformations.

The most popular methods for the synthesis of 4-amino tetrahydropyran ring involve the reaction a substituted aryl aldehyde and homoallylic alcohols and acetonitrile, but many of these methods involve the use of expensive reagent, harsh conditions, extended reaction times, and also require tedious work-up leading to the generation of a large amount of toxic waste. Consequently, there is a need to develop new methods to synthesize these compounds. In our attempt to develop new catalyst system, herein, we describe a mild and efficient procedure to produce 4-amino tetrahydropyran ring derivative in excellent yields in a short reaction time with high selectivity via coupling reaction of 4-chlorobenzaldehyde with 3-en-1-ol in acetonitrile in the presence of iodine and acetyl chloride at room temperature. The reaction was completed in 6.5 hr and the product, 4-acetamido tetrahydro-23. pyrans 3a was obtained in 92% yield with cis-selectivity (Scheme I).

Results and Discussion

An efficient Prins-Ritter reaction sequence for the direct synthesis of 4-amido tetrahydropyrans from homoallylic alcohols, carbonyl compounds and nitriles have been described. Firstly, a three-component coupling reaction of 4-chlorobenzaldehyde with but-3-en-1-ol in acetonitrile in the presence of 20 mol % iodine and equimolar acetyl chloride at RT has been carried out. The reaction went...
to completion in 7 hr and the product, 4-acetamido tetrahydropyran 3a was obtained in 92% yield with cis-selectivity (Scheme I).

Other Lewis acid catalysts such as zinc(II) chloride, ferric chloride hexahydrate, stannous chloride, potassium hydrogen sulphate, and phosphotungstic acid were tested, but I$_2$ was found to be the most efficient in terms of conversion. Thus encouraged, various substituted aryl aldehydes and homoallylic alcohols were examined for the synthesis of 4-acetamido tetrahydropyrans. 4-Chlorobenzaldehyde, 2,4-dichlorobenzaldehyde, 4-nitrobenzaldehyde, 3-nitrobenzaldehyde, 4-methylbenzaldehyde, 4-bromobenzaldehyde, 4-methoxybenzaldehyde reacted well with 3-buten-1-ol and acetonitrile to produce the corresponding 4-acetamido tetrahydropyrans in high yields (Table I, entries b-i). Aliphatic aldehyde (propionaldehyde) also reacted with buten-1-ol and acetonitrile to afford the product in 81% yield (Table I, entry i). Furthermore, substituted homoallylic alcohol such as 1-phenylbut-3-en-1-ol, 1-(3-nitrophenyl)but-3-en-1-ol, 1-(4-chlorophenyl)but-3-en-1-ol and 1-(2,4-dichlorophenyl)but-3-en-1-ol also participated in this transformation (Table I, entries j-o). Ketones such as cyclohexanone and cyclopentanone reacted comparably gave spirocyclic 4-acetamido tetrahydropyrans in good yields (Table I, entries p and q, Scheme II).

The reactions were clean and the products were obtained in excellent yields with high diastereoselectivity as determined from the NMR spectra of the products. In all cases, cis-isomer was obtained exclusively and the structure of which was confirmed by NOE experiments. The formation of the products can be explained by hemi-acetal formation followed by Prins-cyclization and subsequent Ritter amidation (Scheme III).

The structures of compounds 3a-q were characterized by spectral and elemental analysis. Compound 3k showed peaks at 3280, 1642 and 1121 cm$^{-1}$ indicating the presence of -NH-, -CO and –C-O-C- groups in the IR spectrum. A singlet at 3.182 and a doublet at 7.90 (D$_2$O exchangeable) in the $^1$H NMR and signals at δ 23.2 and 168.9 in the $^{13}$C NMR spectrum confirmed the presence of acetamide group in the molecule. The mass spectral data and elemental analysis also supported the structural assignment. The cis stereochemistry was confirmed by NOE.

A rationale for the cis selectivity could be explained by assuming the formation of an (E)-oxocarbenium ion via a chair-like transition state, which has an increased stability relative to the open oxocarbenium ion due to delocalization. The optimal geometry for this delocalization places the hydrogen atom at C4 in a pseudo-axial position, which favours equatorial attack of the nucleophiles $^{23}$.

The structure 3k shown in Table I was deduced from the NMR data, where the two substituents are shown to be cis to each other. The H2 proton has a large and small coupling of $J = 11.2$ Hz. Presence of the large coupling indicates that it is in axial position, with large diaxial coupling with H3a, which imply an equatorial position for the aromatic group at C2. Similarly the equatorial orientation of the substituent at C4 is suggested by the multiplicities of H3a and H5a protons [H3a (q) with $J$ = 11.9 Hz and H5a (dq) with $J = 4.8, \sim 11.9$ Hz].

**Conclusion**

In summary, an efficient Prins-Ritter reaction to produce highly substituted 4-acetamidotetrahydropyrans in high yields with all cis selectivity has been described. The use of inexpensive and readily available iodine makes this procedure simple, convenient and practical. In addition to its simplicity, efficiency and milder reaction conditions, this method provides an easy access for 4-acetamidotetrahydropyrans derivatives with diverse substituent.

**Experimental Section**

Zinc(II) chloride, ferric chloride hexahydrate, stannous chloride and potassium hydrogen sulphate were obtained from S. D. Fine Chemicals. Iodine and
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<th>Entry</th>
<th>Homoallyl alcohol 1</th>
<th>Carbonyl compd 2</th>
<th>Acetamidopyrans(^a)</th>
<th>Time (hr)</th>
<th>Yield (%)(^b)</th>
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*Contd*
phosphotungstic acid was purchased from Aldrich. Reagent grade acetonitrile was used. All melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer. $^1$H and $^{13}$C NMR spectra were recorded in DMSO-$d_6$ using TMS as internal standard on a Jeol spectrometer at 500 MHz and 125 MHz respectively. Mass spectra were recorded on a Jeol DX 303 HF spectrometer. Elemental analyses were recorded using a Thermo Finnigan FLASH EA 1112 CHN analyzer. Column
chromatography was performed over silica gel (100-200 mesh, SRL, India). Analytical TLC were run on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Macherey-Nagel, Germany).

**General procedure for the synthesis of acetamidotetrahydropyrans, 3a-q**

A mixture of homoallylic alcohol (1.0 mmol), carbonyl compound (1.0 mmol), iodine (20 mol %) and acetyl chloride (10 mmol) in acetonitrile (5 mL, used as a solvent) was stirred at RT for a specified time (Table I). After completion of the reaction as indicated by TLC, the reaction mixture was quenched with sodium thiosulfate and extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\). Removal of solvent followed by purification over silica gel (Merck, 100-200 mesh, ethyl acetate-hexane, 4:6) gave pure 4-acetamidotetrahydropyran.

**Spectral data**

\(N\)-[2-(4-Chlorophenyl)-tetrahydropyran-4-yl]-acetamide, 3a

White solid. Isolated Yield: 92%, m.p. 177-79°C. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) 1.16 (q, 1H, \(J = 11.5\) Hz), 1.37 (m, 1H), 1.70 (m, 4H), 1.91 (d, 1H, \(J = 13\) Hz), 3.49 (t, 1H, \(J = 12.3\) Hz), 3.89 (m, 2H), 4.34 (d, 1H, \(J = 10.7\) Hz), 7.28 (m, 4H), 7.84 (d, 1H, \(J = 7.65\) Hz); \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta\) 23.2, 32.6, 46.0, 66.8, 77.4, 122.7, 128.6, 132.1, 142.1, 168.9; IR: 3287, 2930, 2845, 1643, 1563, 1362, 1148, 1090, 830 cm\(^{-1}\); MS (ESI): \(m/z\) 254 (M+1 ion). Anal. Calcd for C\(_{13}\)H\(_{16}\)NO\(_2\)Cl: C, 61.54; H, 6.36; N, 5.52. Found: C, 61.75; H, 6.40; N, 5.58%.

\(N\)-[2-(2-Naphthalen-2-yl-tetrahydropyran-4-yl)-acetamide, 3b

Pale yellow solid. Yield: 88%, m.p. 154-56°C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.52 (m, 2H), 1.89 (s, 3H), 2.03 (m, 1H), 2.32 (m, 1H), 3.76 (m, 1H), 4.23 (m, 1H), 4.24 (m, 1H), 4.56 (dd, 1H, \(J_1 = 3.4\) Hz, \(J_2 = 13.0\) Hz), 5.46 (d, 1H, \(J = 8.4\) Hz), 7.47 (m, 3H), 7.59 (m, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 23.2, 32.9, 40.3, 47.1, 67.4, 78.7, 124.1, 124.6, 125.9, 126.8, 127.4, 128.3, 133.0, 134.1, 139.8, 169.9; IR: 3276, 3048, 2943, 1639, 1550, 1372, 1250, 1145, 1089, 964 cm\(^{-1}\); MS (ESI): \(m/z\) 270 (M+1 ion). Anal. Calcd for C\(_{17}\)H\(_{19}\)NO\(_2\): C, 75.81; H, 7.11; N, 5.20. Found: C, 76.09; H, 7.16; N, 5.17%.

\(N\)-[2-(2,4-Dichlorophenyl)-tetrahydropyran-4-yl]-acetamide, 3c

White solid. Isolated Yield: 86%, m.p. 153-55°C. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) 1.07 (q, 1H, \(J =

\[\text{Scheme II}\]

\[\text{Scheme III}\]
N-[2-(4-Nitrophenyl)-tetrahydropyran-4-yl]-acetamide, 3d

White solid. Isolated Yield: 87%, m.p. 164-66°C. ¹H NMR (500 MHz, DMSO-d₆): δ 1.14 (q, 1H, J = 11.5 Hz), 1.40 (m, 1H), 1.71 (m, 4H), 1.99 (d, 1H, J = 12.2 Hz), 3.52 (t, 1H, J = 12.2 Hz), 3.93 (m, 1H), 4.02 (dd, 1H, J₁ = 3.85 Hz, J₂ = 11.5 Hz), 4.52 (d, 1H, J = 10.0 Hz), 7.55 (d, 2H, J = 8.4 Hz) 7.97 (d, 1H, J = 7.7 Hz), 8.14 (d, 2H, J = 8.4 Hz); ¹³C NMR (125 MHz, DMSO-d₆): δ 23.8, 32.6, 39.3, 44.8, 68.4, 74.3, 126.8, 128.3, 129.7, 131.8, 132.9, 139.6, 168.4; IR: 3288, 2922, 2858, 1672, 1519, 1425, 1345, 1148, 1084, 854 cm⁻¹; MS (ESI): m/z 288 (M+1 ion). Anal. Calcd for C₁₃H₁₂NO₂Cl: C, 54.18; H, 5.25; N, 4.86. Found: C, 54.39; H, 5.29; N, 4.81%.  

N-[2-(4-Bromophenyl)-tetrahydropyran-4-yl]-acetamide, 3g
White solid. Yield: 86%, m.p. 176-78°C. ¹H NMR (500 MHz, CDCl₃): δ 0.96 (t, 3H, J = 7.5 Hz), 2.19 (m, 2H), 3.69 (m, 1H ), 4.10 (m, 2H), 4.36 (dd, 1H, J₁ = 2.2 Hz, J₂ = 11.6 Hz), 5.21 (d, 1H, J = 7.7 Hz), 7.19 (d, 2H, J = 8.4 Hz) 7.49 (d, 2H, J = 8.4 Hz ); ¹³C NMR (125 MHz, CDCl₃): δ 11.6, 18.7, 32.8, 39.6, 40.7, 47.1, 69.1, 77.9, 122.3, 128.4, 132.6, 142.1, 173.2; IR: 3926, 2956, 2849, 1648, 1560, 1268, 1096, 741 cm⁻¹; MS (ESI): m/z 327 (M+1 ion). Anal. Calcd for C₁₃H₁₂BrNO₂: C, 55.23; H, 6.18; N, 4.29. Found: C, 55.46; H, 6.23; N, 4.32%.  

N-[2-(4-Methoxyphenyl)-tetrahydropyran-4-yl]-acetamide, 3h
Pale green solid. Yield: 79%, m.p. 182-84°C. ¹H NMR (500 MHz, CDCl₃): δ 1.36 (q, 1H, J = 12.5 Hz), 1.39 (m, 1H), 1.98 (s, 3H), 2.10 (m, 1H), 2.16 (m, 1H), 3.69 (m, 1H), 3.78 (s, 3H), 4.17 (m, 2H), 4.33 (dd, 1H, J₁ = 2.2 Hz, J₂ = 11.8 Hz), 5.36 (dd, 1H, J = 7.7 Hz, 6.96 (d, 2H, J = 8.4 Hz ), 7.18 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 23.1, 41.4, 43.1, 46.7, 54.7, 56.9, 74.1, 114.8, 129.1, 134.3, 156.8, 169.4; IR: 3341, 2956, 2937, 1649, 1561, 1371, 1079, 1043, 814, 733 cm⁻¹; MS (ESI): m/z 250 (M+1 ion). Anal. Calcd for C₁₃H₁₂NO₂: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.63; H,7.71; N, 5.66%.  

N-(2-p-Tolyltetrahydropyran-4-yl)-acetamide, 3f
White solid. Yield: 88%, m.p. 163-65°C. ¹H NMR (500 MHz, CDCl₃): δ 1.43 (m, 2H), 1.90 (s, 3H), 1.98 (m, 1H), 2.21 (m, 1H), 2.36 (s, 3H), 3.65 (m, 1H), 4.17 (m, 2H), 4.37 (dd, 1H, J₁ = 3.1 Hz, J₂ = 12.6 Hz), 5.46 (d, 1H, J = 8.4 Hz), 7.73 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 21.6, 21.9, 23.4, 26.1, 34.0, 40.6, 42.8, 126.3, 128.3, 169.3; IR: 3288, 2957, 2938, 1651, 1556, 1371, 1096, 1042, 871, 730 cm⁻¹; MS (ESI): m/z 256 (M+Na ion). Anal. Calcd for C₁₉H₁₇NO₂: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.37; H, 8.26; N, 6.02%.  

N-(2,6-Diphenyltetrahydropyran-4-yl)-acetamide, 3j
Pale yellow solid. Isolated Yield: 84%, m.p. 220-22°C. ¹H NMR (500 MHz, DMSO-d₆): δ 1.32 (q, 2H, J = 11.7 Hz), 1.80 (s, 3H), 2.04 (m, 2H), 4.14 (m, 1H), 4.64 (d, 2H, J = 10.2 Hz), 7.27 (m, 10H), 7.90 (d, 1H, J = 7.5 Hz); ¹³C NMR (125 MHz, DMSO-d₆):
δ 22.7, 45.8, 77.3, 125.6, 127.2, 128.2, 142.5, 168.5. IR: 3280, 3070, 2842, 1642, 1553, 1374, 1293, 1121, 748, 697 cm⁻¹; MS (ESI): m/z 296 (M+1 ion). Anal. Calcd for C₁₉H₂₁NO₂: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.47; H, 7.21; N, 4.69%.

**N-[2-(4-Bromophenyl)-6-phenyltetrahydropyran-4-yl]-acetamide, 3k**

Pale yellow solid. Yield: 83%, m.p. 169-72°C. ¹H NMR (500 MHz, CDCl₃): δ 1.30 (m, 2H), 1.79 (s, 3H), 2.36 (m, 2H), 4.39 (m, 1H), 4.62 (m, 2H), 5.39 (d, 1H, J = 7.7 Hz), 7.30 (m, 5H), 7.46 (m, 2H), 7.52 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 23.2, 40.8, 42.6, 47.8, 58.1, 79.2, 128.5, 128.9, 130.6, 132.1, 141.6, 142.9, 143.2, 169.9; IR: 3231, 2956, 2846, 1656, 1548, 1536, 1078, 946, 813, 736 cm⁻¹; MS (ESI): m/z 375 (M+1 ion). Anal. Calcd for C₂₀H₁₇BrNO: C, 56.47; H, 5.40; N, 3.74. Found: C, 56.10; H, 5.40; N, 3.76%.

**N-[2-(3-Nitrophenyl)-6-phenyltetrahydropyran-4-yl]-acetamide, 3l**

White solid. Yield: 82%, m.p. 169-72°C. ¹H NMR (500 MHz, CDCl₃): δ 1.30 (q, 2H, J = 7.7 Hz), 1.79 (s, 3H), 2.02 (m, 2H), 4.12 (m, 1H), 4.94 (m, 2H), 7.23 (m, 3H), 7.40 (m, 4H), 8.23 (d, 1H, J = 8.4 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 23.2, 36.8, 42.7, 63.1, 74.6, 122.3, 129.6, 129.8, 132.1, 132.8, 133.9, 134.3, 137.1, 138.2, 139.3, 147.6, 169.4; IR: 3231, 2956, 2846, 1656, 1548, 1536, 1078, 946, 813, 736 cm⁻¹; MS (ESI): m/z 375 (M+1 ion). Anal. Calcd for C₁₉H₁₇NO₃: C, 67.29; H, 5.98; N, 8.27%.

**References**