1,2-Addition of Allyl and 2-Oxo-2*H*-pyran-6-ylcarbonyl Groups to Cyclic C=N Double Bonds by Means of Organotin Reagent for Alkaloids Synthesis; A Facile Synthesis of 8-Oxoprotoberberine and Norketoyobirine (Demethoxycarbonyloxogambirtannine)[1]

Ryohei YAMAGUCHI,* Atsuo OTSUJI,† Kiitiro UTIMOTO,† and Sinpei KOZIMA
Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University, Yoshida, Kyoto 606
† Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606
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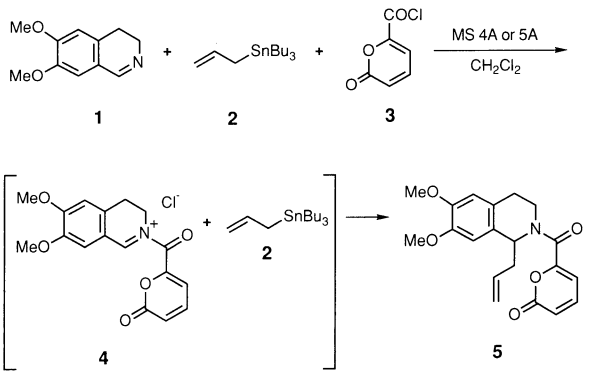
Synopsis. 1,2-Introduction of allyl and 2-oxo-2*H*-pyran-6-ylcarbonyl groups into isoquinoline system can be effectively accomplished by reaction of allyltributyltin with 3,4-dihydroisoquinoline activated by 2-oxo-2*H*-pyran-6-ylcarbonyl chloride. Allyltributyltin reacts similarly with 3,4-dihydro-β-carboline activated by 2-oxo-2*H*-pyran-6-ylcarbonyl chloride to give the corresponding 1,2-adduct. Intramolecular Diels–Alder reactions of the 1,2-adducts followed by DDQ oxidations afford 8-oxoprotoberberine and norketoyobirine.

Development of methodologies for effective introduction of useful carbon substituents into nitrogen heterocycles is valuable for constructing nitrogen polycyclic compounds related to alkaloids. We have reported that several kinds of organotin reagents readily react with cyclic C=N double bonds activated by chloroformate esters or acyl chlorides, making it possible to introduce allyl, 1-alkynyl, 2-alkynyl, and benzyl groups into pyridine, isoquinoline, and quinoline rings chemo- and regioselectively.[2] We have also uncovered organotin-aided simultaneous introduction of allyl and α,β:γ,δ-unsaturated acyl groups[3] or 2,4-pentadienyl and α,β-unsaturated acyl groups[4] into isoquinoline and/or 3,4-dihydro-β-carboline systems and the subsequent intramolecular Diels–Alder cycloadditions to afford pseudo-berbane, allo-berbane, and allo-yohimbane systems stereoselectively, providing a highly effective methods for synthesis of nitrogen polycyclic compounds related to alkaloids. We report here that a facile 1,2-addition of allyl and 2-oxo-2*H*-pyran-6-ylcarbonyl groups to cyclic C=N bonds can be accomplished by means of organotin reagents and that the resulting 1,2-adducts can be readily converted to protoberberine[5] and aromatic yohimbane systems[6,7]

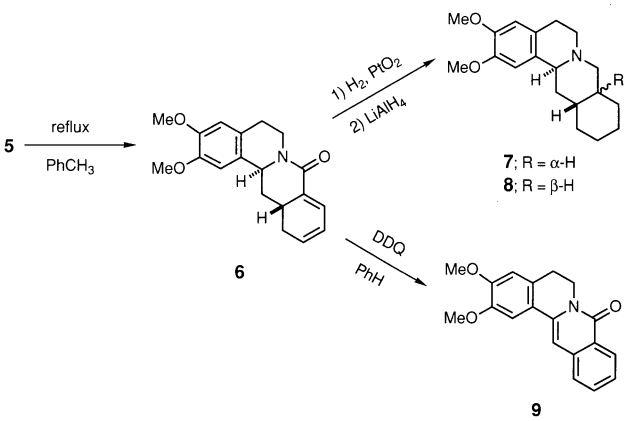
When 2-oxo-2*H*-pyran-6-ylcarbonyl chloride (**3**) was added to a mixture of 6,7-dimethoxy-3,4-dihydroisoquinoline (**1**) and allyltributyltin (**2**) in dichloromethane in the presence of molecular sieves (MS) 4A or 5A, the coupling reaction of the three components proceeded nicely through the *N*-acyliminium salt (**4**) to give the 1,2-adduct (**5**) in 90—97% isolated yield (Scheme 1).[8] The presence of MS is preferable in order to obtain the high yield of **5**.[9]

As expected by the fact that 2-oxo-2*H*-pyran-6-ylcarbonyl group serves as a good enophile in the inverse electron demand Diels–Alder reactions,[10,11] the subsequent intramolecular Diels–Alder reaction of **5** followed by decarboxylation took place smoothly upon heated at reflux in toluene to afford a tetracyclic compound (**6**) in 94% yield (Scheme 2).[12] Catalytic hydrogenation of **6** followed by hydride reduction gave a mixture of (±)-pseudo- and (±)-epiallo-7,8-dimethoxyberbanes (**7** and **8**) in a ratio of ca. 2:1, confirming the stereochemistry of **6**. Furthermore, dehydrogenation of **6** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) afforded the known 2,3-dimethoxy-8-oxoprotoberberine (**9**)[7,13] in 90% yield.

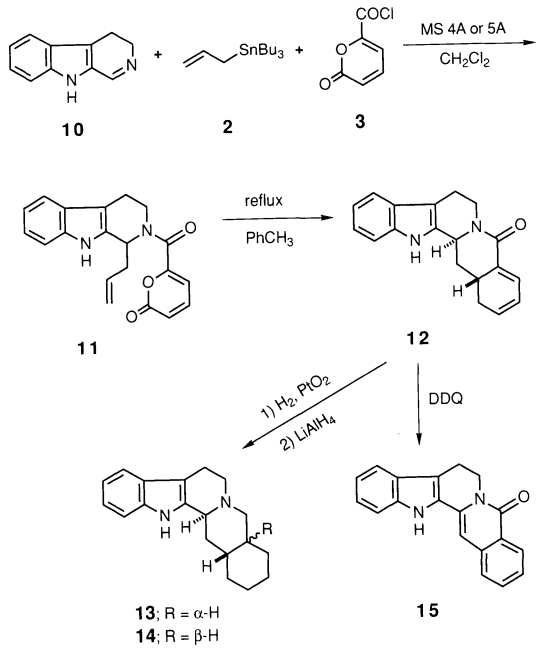
We next examined a synthesis of yohimbane system by the similar methodology to the above. Thus, the coupling reaction of 3,4-dihydro-β-carboline (**10**) activated by **3** with **2** readily proceeded in the presence of MS 4A or 5A to afford the 1,2-adduct (**11**) in 75—82% yield.[14] The subsequent intramolecular Diels–Alder reaction of **11** followed by decarboxylation gave a pentacyclic compound (**12**) in 88% yield. The stereochemistry of **12** was confirmed by the fact that catalytic hydrogenation of **12** followed by hydride reduction gave a mixture of (±)-pseudo- and (±)-epiallo-



Scheme 1.



Scheme 2.



Scheme 3.

yohimbanes (**13** and **14**) in a ratio of 3:1. Dehydrogenation of **12** with DDQ furnished norketoyobirine (**15**)[13e,15] in 75% yield.

In summary, we have demonstrated an effective method for 1,2-introduction of allyl and 2-oxo-2*H*-pyran-6-ylcarbonyl groups into nitrogen heterocycles by means of organotin reagent. The subsequent inverse electron demand intramolecular Diels-Alder reactions proceeds smoothly to give polycyclic compounds, from which protoberberine and aromatic yohimbane systems can be readily synthesized.

Experimental

Melting points were measured on a Yanagimoto hot-plate apparatus and were uncorrected. The IR spectra were obtained on a JASCO IR-80 spectrometer. The ^1H NMR spectra were taken on Varian EM-390 and XL-200 spectrometers, tetramethylsilane (TMS) being chosen as the internal standard. The ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer, TMS being chosen as the internal standard. The microanalyses were performed by Kyoto University Elemental Analysis Center. The compounds, **1**,[16] **3**,[17] and **10**[18] were prepared according to the literature procedures. Dichloromethane was distilled from P_2O_5 before use. All the reactions were carried out under an Ar atmosphere, unless otherwise noted.

(±)-1-Allyl-6,7-dimethoxy-2-(2-oxo-2*H*-pyran-6-ylcarbonyl)-1,2,3,4-tetrahydroisoquinoline (5). To a mixture of **1** (185 mg, 0.97 mmol), **2** (340 mg, 1.03 mmol), and MS 5A (0.50 g) in CH_2Cl_2 (3 cm³) was added **3** (165 mg, 1.04 mmol) under ice-cooling. The mixture was stirred at room temp for 3.5 h. The solvent was evaporated and the residue was chromatographed on silica gel. Elution by CH_2Cl_2–AcOEt (9:1) gave **5** (336 mg, 97%) which gradually solidified. **5**: Mp 111—113 °C; IR (neat) 1740, 1640, 1515 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.45 (dd, 1H, J = 7 and 9 Hz), 6.57—6.78 (m, 3H), 6.42 (d, 1H, J = 9 Hz), 5.43—6.26 (m, 2H), 4.97—5.28 (m,2H), 3.87 (s, 6H), 2.55—3.80 (m, 6H); ^{13}C NMR ($CDCl_3$) δ = 160.6 (s), 159.7 (s), 155.9 (s), 148.1 (s), 147.7 (s), 143.0 (d), 134.4 (d), 127.7 (s), 125.1 (s), 117.7 (t), 117.4 (d), 111.5 (d), 110.1 (d), 106.7 (d), 56.0 (q), 55.9 (q), 52.7 (d), 50.0 (2t), 28.8 (t).

(±)-(12a*R, 13a*S**)-5,6,12,12a,13,13a-Hexahydro-2,3-dimethoxy-8*H*-dibenzo[*a,g*]quinolizin-8-one (6).** A solution of **5** (484 mg, 1.36 mmol) in $PhCH_3$ (27 cm³) containing a small amount of 2,6-di-*t*-butylphenol was heated at reflux for 24 h. The solvent was evaporated and the residue was chromatographed on silica gel. Elution by CH_2Cl_2–AcOEt (9:1) gave **6** (397 mg, 94%) which gradually solidified. **6**: Mp 148—151 °C; IR (neat) 1641, 1612, 1560 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 6.98—7.05 (m, 1H), 6.68 (s, 1H), 6.66 (s, 1H), 6.07—6.18 (m, 2H), 4.80—4.92 (m, 1H), 4.73 (t,1H, J = 5 Hz), 3.88 (s, 3H), 3.87 (s, 3H), 2.62—3.10 (m, 4H), 1.95—2.48 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 164.9 (s), 148.2 (s), 147.6 (s), 131.0 (d), 129.6 (d), 129.0 (s), 128.4 (s), 128.1 (s), 125.0 (d), 112.2 (d), 108.0 (d), 56.3 (q), 55.9 (q), 54.6 (d), 41.8 (t), 33.3 (t), 30.2 (t), 28.4 (d), 28.3 (t). Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80%. Found: C, 73.06; H, 6.76%.

Reduction of 6 to (±)-Pseudo- and (±)-Epiallo-7,8-dimethoxyberbanes (7 and 8). A mixture of **6** (448 mg, 1.44 mmol) and PtO_2 (48 mg) in MeOH (40 cm³) was stirred under a H_2 atmosphere. After the reaction was complete, PtO_2 was filtered off through Celite and the solvent was evaporated to give hydrogenated products (420 mg, 92%). The hydrogenated products (150 mg, 0.48 mmol) was dissolved in THF–Et_2O (1:1, 10 cm³) and $LiAlH_4$ (162 mg, 4.27 mmol) was added to the solution. The mixture was heated at reflux for 6 h. Usual work-up and column chromatography on Al_2O_3 (CH_2Cl_2) gave a mixture of **7** and **8** (total 59 mg) and pure **7** (31 mg). The total yield was 62% and the ratio of **7** to **8** was determined to be 2:1 by ^1H NMR analysis. A mixture of **7** and **8** was further chromatographed on Al_2O_3 (hexane/CH_2Cl_2 = 1/1) to give a small amount of pure **8**. ^1H and ^{13}C NMR spectra of **7** were identical with those of the authentic sample[4] and ^1H NMR spectrum of **8** was essentially identical to the reported one.[19] **8**: ^1H NMR ($CDCl_3$) δ = 6.69 (s, 1H), 6.59 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.32 (br d, 1H, J = 12 Hz), 2.90—3.24 (m, 2H), 2.45—2.78 (m, 4H), 1.23—2.27 (m, 12H); ^{13}C NMR ($CDCl_3$) δ = 147.3 (s), 147.1 (s), 130.8 (s), 127.0 (s), 111.6 (d), 108.3 (d), 57.3 (d), 56.0 (q), 55.8 (t), 52.8 (t), 37.7 (t), 34.8 (d), 34.4 (d), 29.6 (t), 29.2 (t), 26.8 (t), 26.4 (t), 21.7 (t).

2,3-Dimethoxy-5,6-dihydro-8*H*-dibenzo[*a,g*]quinolizin-8-one (9). A mixture of **6** (127 mg, 0.39 mmol) and DDQ (181 mg, 0.80 mmol) in PhH (3 cm³) was heated at reflux for 27 h. Usual work-up and column chromatography on silica gel gave **9** (107 mg, 90%). ^1H NMR spectrum of **9** was essentially identical to the reported one.[13b,13c] **9**: ^1H NMR ($CDCl_3$) δ = 8.48 (d, 1H, J = 7 Hz), 7.43—7.73 (m, 3H), 7.32 (s, 1H), 6.93 (s, 1H), 6.79 (s, 1H), 4.41 (t, 2H, J = 6 Hz), 4.03 (s, 3H), 3.97 (s, 3H), 2.97 (t, 2H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ = 162.2 (s), 150.4 (s), 148.6 (s), 137.3 (s), 136.7 (s), 132.2 (s), 128.7 (s), 127.9 (d), 126.1 (d), 125.9 (d), 124.5 (s), 122.2 (s), 110.5 (d), 108.0 (d), 101.5 (d), 56.3 (q), 56.0 (q), 39.7 (t), 28.0 (t).

(±)-1-Allyl-2-(2-oxo-2*H*-pyran-6-ylcarbonyl)-1,2,3,4-tetrahydro-β-carboline (11). To a mixture of **10** (849 mg, 5.00 mmol), **2** (3310 mg, 10.0 mmol), and MS 5A (1.00 g) in CH_2Cl_2 (5 cm³) was added **3** (805 mg, 5.1 mmol) at once under ice-cooling. The reaction mixture was stirrred for 17 h at room temp and chromatographed on silica gel. Elution by CH_2Cl_2 and then CH_2Cl_2–AcOEt (9:1) gave **11** (1361 mg, 82%): IR (neat) 1735, 1640, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 8.50 (br s, 1H), 7.00—7.54 (m, 5H), 6.60 (d, 1H, J = 8 Hz), 6.37 (d, 1H, J = 9 Hz), 5.55—6.17 (m, 2H), 5.00—5.30 (m, 2H), 2.53—4.20 (m, 6H); ^{13}C NMR ($CDCl_3$) δ = 161.1 (s), 159.8 (s), 155.5 (s), 143.0 (d), 136.2 (s), 133.7 (d), 132.4 (s), 126.4 (s), 122.0 (d), 119.5 (d), 118.7 (t), 118.1 (d), 117.6 (d), 111.1 (d), 107.7 (s), 106.7 (d), 50.4 (d), 42.3 (t), 38.7 (t), 22.2 (t).

(±)-(13b*S,14a*R**)-5,7,8,13,13b,14,14a-Hexahydro-**

benz[*g*]indolo[2,3-*a*]quinolizin-5(1*H*)-one (12). A solution of **11** (1361 mg, 4.07 mmol) in $PhCH_3$ (50 cm^3) was heated at reflux for 42 h. The solvent was evaporated and the residue was chromatographed on silica gel. Elution by CH_2Cl_2–AcOEt (9:1) gave **12** (1041 mg, 88%): Mp 234—238 °C; IR (Nujol) 1645, 1595, 1560 cm^{-1}; ^1H NMR (DMSO-d_6) δ = 7.28—7.48 (m, 2H), 6.92—7.14 (m, 2H), 6.83 (br s, 1H), 6.00—6.18 (m, 2H), 5.02 (br s,1H), 4.78 (dd, 1H, J = 12 and 5 Hz), 3.05 (td, 1H, J = 12 and 5 Hz), 1.93—2.90 (m, 7H); ^{13}C NMR (DMSO-d_6) δ = 163.7 (s), 135.7 (s), 134.3 (s), 131.3 (d), 129.1 (s), 128.7 (d), 126.7 (s), 124.3 (d), 120.8 (d), 118.5 (d), 117.5 (d), 111.1 (d), 108.1 (s), 52.4 (d), 42.5 (t), 30.4 (t), 29.6 (t), 28.6 (d), 20.4 (t). Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25%. Found: C, 78.58; H, 6.19%.

Reduction of 12 to (±)-Pseudo- and (±)-Epiallo-yohimbanes (13 and 14). A mixture of **12** (120 mg, 0.41 mmol) and PtO_2 in MeOH (40 cm^3) was stirred under H_2 atmosphere. After the rection was complete, PtO_2 was filtered off and the solvent was evaporated to give hydrogenated products (115 mg, 95%). The hydrogenated products (99 mg, 0.33 mmol)was dissolved in THF (12 cm^3) and $LiAlH_4$ (145 mg, 3.82 mmol) was added to the solution. The mixture was heated at reflux for 3.5 h. Usual work-up and column chromatography on Al_2O_3 (hexane–CH_2Cl_2, 4 : 1) gave pure **13** (27 mg) and **14** (10 mg), and a mixture of **13** and **14** (total 21 mg). The total yield was 62% and the ratio of **13** to **14** was determined to be 3 : 1 by ^1H NMR analysis. ^1H and ^{13}C NMR spectra of **13** and **14** were essentially identical to the reported ones.[20,21] **13**: ^1H NMR ($CDCl_3$) δ = 7.85 (br s, 1H), 7.51—7.60 (m, 1H), 7.37—7.45 (m, 1H), 7.11—7.28 (m, 2H), 4.46—4.55 (m, 1H), 3.25—3.38 (m, 2H), 2.95—3.23 (m, 1H), 2.39—2.63 (m, 3H), 0.69—2.10 (m, 12H); ^{13}C NMR ($CDCl_3$) δ = 135.5 (s), 133.5 (s), 127.9 (s), 121.3 (s), 119.4 (d), 118.0 (d), 110.8 (d), 107.9 (s), 54.1 (d), 51.8 (t), 51.3 (t), 41.7 (d), 36.2 (d), 35.1 (t), 32.9 (t), 30.3 (t), 26.2 (t), 25.9 (t), 16.9 (t). **14**: ^1H NMR ($CDCl_3$) δ = 7.82 (br s, 1H), 7.47—7.58 (m, 1H), 7.27—7.37 (m, 1H), 7.06—7.22 (m, 2H), 3.40—3.59 (m, 1H), 2.93—3.17 (m, 2H), 2.57—2.87 (m, 4H), 1.22—2.32 (m, 12H); ^{13}C NMR ($CDCl_3$) δ = 136.0 (s), 135.4 (s), 127.5 (s), 121.1 (d), 119.3 (d), 118.0 (d), 110.7 (d), 108.3 (s), 55.1 (t), 54.5 (d), 53.4 (t), 35.8 (t), 34.8 (t), 34.1 (t), 29.6 (t), 26.6 (t), 26.4 (t), 21.8 (t), 21.6 (t).

8,13-Dihydrobenz[*g*]indolo[2,3-*a*]quinolizin-5(7*H*)-one (15). A mixture of **12** (158 mg, 0.54 mmol) and DDQ (266 mg, 1.17 mmol) in THF (20 cm^3) was heated at reflux for 20 h. The solvent was evaporated and the residue was chromatographed on silica gel. Elution by CH_2Cl_2—AcOEt (9 : 1) gave **15** (117 mg, 75%). ^1H NMR spectrum of **15** was essentially identical to the reported one.[15b] **15**: ^1H NMR (DMSO-d_6) δ = 8.28 (d, 1H, J = 7 Hz), 7.42—7.83 (m, 5H), 7.05—7.35 (m, 3H), 4.42 (t, 2H, J = 7 Hz), 3.10 (t, 2H, J = 7 Hz); ^{13}C NMR (DMSO-d_6) δ = 161.2 (s), 138.0 (s), 136.1 (s), 132.4 (d), 132.3 (s), 128.1 (s), 127.4 (d), 126.0 (d), 125.8 (d), 125.5 (s), 124.5 (s), 123.4 (d), 119.4 (d), 119.0 (d), 112.4 (s), 111.5 (d), 99.0 (d), 26.2 (t), 19.3 (t).

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8) It has been reported that the reaction of **1** with **3** and allyltrimethylsilane in the presence of $AgBF_4$ gave **5** in 64% yield.[7]

9) Without MS 4A or 5A, the yield varied less than 90%. MS probably removes a trace amount of water, because the control experiment in a NMR sample tube has shown that the *N*-acyliminium salt **4** is highly sensitive to water and is readily hydrolyzed by addition of a drop of H_2O to give a compound, whose NMR spectra suggest that its structure may be 4,5-dimethoxy-2[2-[*N*-(2-oxo-2*H*-pyran-6-ylcarbonyl)amino]-ethyl]benzaldehyde: ^1H NMR ($CDCl_3$) δ = 10.22 (s, 1H), 7.49 (dd, 1H, J = 7 and 9 Hz), 7.35 (s, 1H), 7.13 (d, 1H, J = 7 Hz), 6.80 (s, 1H), 6.50 (d, 1H, J = 9 Hz), 3.97 (s, 3H), 3.94 (s, 3H), 3.20—3.90 (m, 4H), 2.45 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ = 190.8 (d), 159.7 (s), 158.5 (s), 153.8 (s), 152.4 (s), 148.1 (s), 143.0 (d), 135.9 (s), 127.2 (s), 119.2 (d), 113.7(d), 113.6 (d), 106.7 (d), 56.3 (q), 56.1 (q), 41.4 (t), 31.7 (t).

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