Refined Protocols for the Preparation of 3-Alkoxy-2,5-dihydrofurans, Allylic Oxidation to β-Alkoxybutenolides and Short Synthesis of (±)-Annularin H

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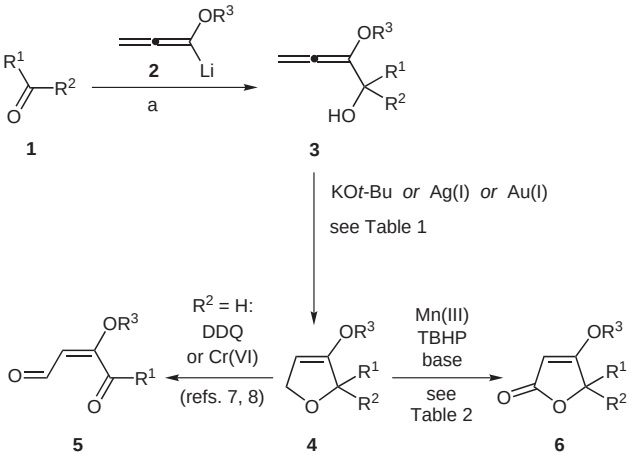
Abstract: The 5-*endo* cyclization of α-allenyl alcohols derived from carbonyl compounds and lithiated alkoxyallenes was reinvestigated by comparing the known reagents KO*t*-Bu, $AgNO_3$ or $AgBF_4$ with the reagent system AuCl/pyridine. A variety of 3-alkoxy-2,5-dihydrofurans **4** was efficiently prepared, in some cases with high diastereoselectivity. These product compounds were subjected to manganese(III)-catalyzed allylic oxidation which led to β-alkoxybutenolides with moderate to good yield. Combination of these newly tuned methods allowed for a concise and short synthesis of (±)-annularin H.

Key words: allenes, gold catalysis, dihydrofurans, allylic oxidation, butenolides

Electrophile-induced 5-*endo-trig* cyclizations of α-allenyl alcohols constitute a well-known and elegant route to synthetically useful 2,5-dihydrofurans. Brønsted acids,[1] bases, e.g. KO*t*-Bu,[2] and Ag(I) salts[3] have been utilized as promoters in these reactions. More recently, the introduction of Au(I)- and Au(III)-based catalysts has set new standards in the 5-*endo* and 6-*endo* cyclizations of various allenic substrates.[4] As part of our ongoing interest in lithiated alkoxyallenes as building blocks for heterocyclic synthesis,[5] we required a new and more general protocol for the 5-*endo* cyclization of alkoxyallene-derived α-allenyl alcohols to 3-alkoxy-2,5-dihydrofurans.[2,6a] Our progress using a Au(I) catalyst is described in this report. Further, we have continuously been aiming for new oxidative transformations of these synthetically valuable intermediates[7,8] and we present first results in their allylic oxidation to β-alkoxybutenolides.

Nucleophilic addition of lithiated alkoxyallenes **2** towards aldehydes and ketones **1** quantitatively furnishes α-allenyl alcohols **3** (purity generally >95% by ^{1}H NMR) and in some cases with high diastereoselectivity (Scheme 1, Table 1).[6a,b] The 5-*endo* cyclization of crude adducts **3** with KO*t*-Bu (0.25–0.50 equiv, DMSO solution, 50–60 °C) was first reported by Brandsma and Arens[2a] and this system operates cleanly for simple substrates (see Table 1, entries 1–3, method **A**). Yields for dihydrofurans **4** typically range between 50% and 85% over two steps and, if diastereomers are employed in the reaction, their ratio is usually preserved (see conversions **1b** → **4b** and **1c** → **4c**).



Scheme 1 Preparation and oxidative transformations of 3-alkoxy-2,5-dihydrofurans **4**, starting from carbonyl compounds **1** and lithiated alkoxyallenes **2**. *Reagents and conditions*: a) Et_2O, –78 °C, 1–4 h.

These harsh conditions do not tolerate siloxy groups, α-aryl substituents and functionalities that undergo elimination, isomerization, or radical[9] side reactions. For instance, α-allenols derived from lithiated methoxyallene and aldehydes **1d**, **1e** and **1f** decomposed or gave modest yields (**1e** → **4e**). On the other hand, allenols **3** incorporating the alkoxyallene moiety prohibit the use of Brønsted acid promoters due to their enol ether reactivity. These severe limitations may be overcome by employing Ag(I) salts. We have previously adopted Claesson's conditions[3a] (10–30 mol% $AgNO_3$ and 1–2 equiv of $CaCO_3$) for the cyclization of allenyl amines derived from alkoxyallenes and *N*-alkyl, *N*-tosyl and *N*-Boc imines.[10] In the case of alcohols **3**, however, this protocol led to rapid decomposition when base was present (K_2CO_3 was used in acetone or in acetonitrile). In the absence of the base, the desired cyclizations proceeded more cleanly but very slowly even at elevated temperatures, and high loading of the metal salt was necessary (25–50 mol% $AgNO_3$ or $AgBF_4$, see entries 4–6, methods **C** and **D**). Thus, TBS-protected dihydrofuran **4d** was isolated in 61% yield over two steps after five days with 50 mol% of $AgNO_3$. The conversion of **4e** was very low even after three days, and the notoriously difficult derivative **4f** did not react cleanly.[7]

Improvements to all of these cyclization processes were overdue and we were pleased that, after some experimentation, gold catalysis ultimately also matched our allenic substrates. We could perform cycloisomerizations of substrates **3** with 5 mol% of AuCl and 15 mol% of pyridine

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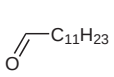
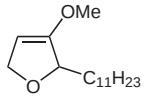
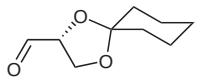
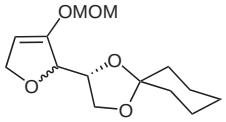
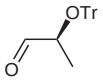
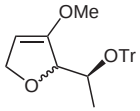
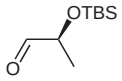
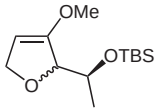
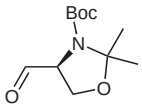
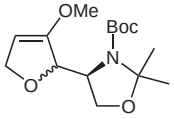
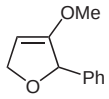
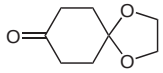
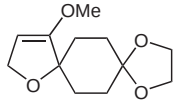
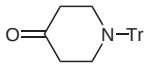
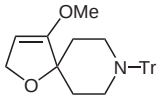
Table 1 Two-Step Preparation of Dihydrofurans **4** Derived from Aldehydes or Ketones **1** and Lithiated Alkoxyallenes (Scheme 1)[a,16]

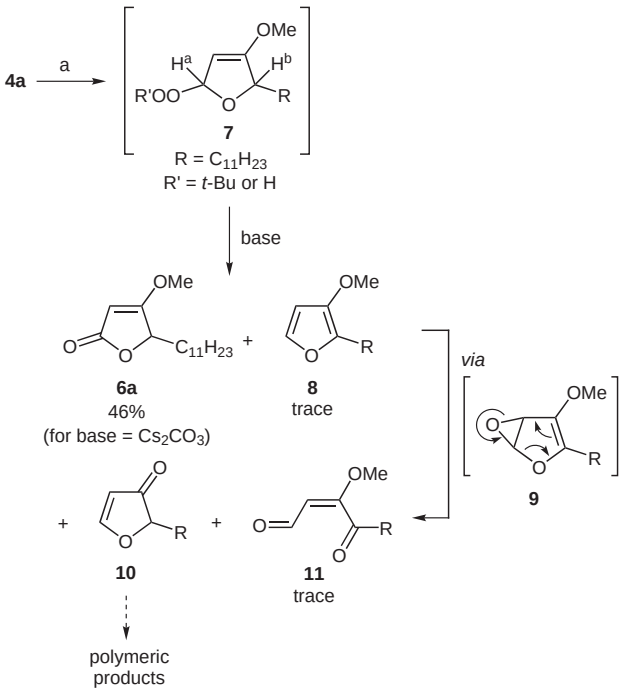
Entry	Electrophile		**2** R^3	dr (adduct **3**)	Cyclization conditions	Yield (%)[b]	Product		dr
1	**1a**		Me	–	**A**	65	**4a**		–
2	**1b**		MOM	65:35 (*anti*/*syn*)	**A**	70	**4b**		67:33
3	**1c**		Me	70:30 (*anti*/*syn*)	**A** **B**	86 70	**4c**		70:30 70:30
4	**1d**		Me	88:12 (*anti*/*syn*)	**A** **B** **C**	dec. 66 61	**4d**		83:17 84:16
5	**1e**		Me	82:18 (*anti*/*syn*)	**A** **B** **D**	37 78 19	**4e**[c]		83:17 82:18 84:16
6	**1f**		Me	–	**A** **B** **C**	mixture 75 31[d]	**4f**		–
7	**1g**		Me	–	**B**	85	**4g**		–
8	**1h**[e]		Me	–	**B**	70	**4h**		–

[a] Conditons **A**: KO*t*-Bu (0.50 equiv), DMSO, 60 °C, 1.5 h. Conditions **B**: AuCl (5 mol%), pyridine (15 mol%), CH_2Cl_2, r.t., 30 min to 3 h. Conditions **C**: $AgNO_3$ (0.25–0.50 equiv), MeCN, r.t. or 50 °C, 1–5 d. Conditions **D**: $AgBF_4$ (0.30 equiv), MeCN, 35 °C to 50 °C, 72 h.
[b] Yield over two steps.
[c] Stereochemistry proven by X-ray crystal structure analysis of the main diastereomer.
[d] Result taken from ref. 7.
[e] Addition reaction performed in THF.

in CH_2Cl_2. These conditions have been reported by Krause for the 6-*endo* cyclization of β-allenyl alcohols to dihydropyrans[4b] (in turn, $AuCl_3$ in CH_2Cl_2[4a] again led to decomposition). Results were now clearly superior to all aforementioned reagent systems, since reactions are complete very rapidly and products are formed with high yields and perfect chemoselectivity (see conversions **1d**–**h** → **4d**–**h**, method **B**). The short reaction time of the gold-catalyzed reaction is a distinct feature – in some cases, conversion was complete after 15–30 min at room temperature. On the other hand, a precatalyst loading of 5 mol% was mandatory since substrates **3** have to be used in the reaction as crude materials (chromatographic purification inevitably leads to decomposition). The purity should be ca. 95% or higher (^{1}H NMR) for the catalyst to operate since no reaction occurred with slightly more impure starting materials.

Oxidative transformations of dihydrofurans **4** lead to multifunctional building blocks which are highly useful intermediates in natural product synthesis. Treatment of substrates **4** with wet DDQ[7,8] or CrO_3–dimethylpyrazole complex yields α,β-unsaturated γ-ketoaldehydes **5** (Scheme 1) which served us as precursors in the synthesis of rare deoxy sugars.[8] Alternatively, their allylic oxidation would furnish unsaturated γ-lactones **6** and we have screened many reagents for this purpose. After some failures, we succeeded in the allylic oxidation by modifying Shing's conditions[11] using TBHP and catalytic amounts of manganese(III) acetate dihydrate (Table 2). When dihydrofuran **4a** was reacted under the exact conditions reported by Shing, we isolated butenolide **6a** in 32% yield, along with several side products and some polymeric material. In the subsequent optimization attempts, we varied solvent, tested basic and acidic additives and the influence

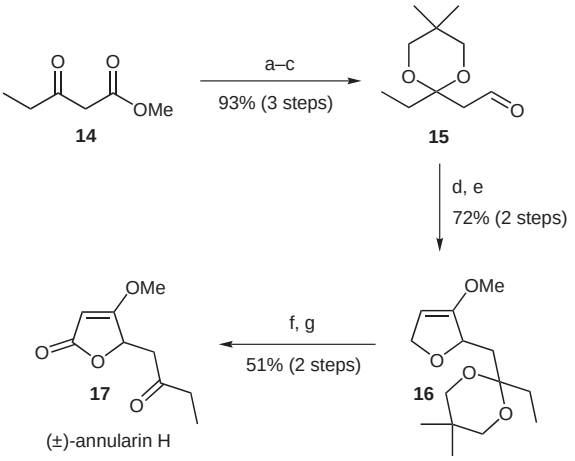
of temperature. These optimizations slightly improved the yield of **6a**, ultimately up to moderate 46%. Under these optimum conditions (solvent MeCN, 0.50 equiv Cs_2CO_3, 4 Å MS, O_2 atmosphere, 0 °C, 72 h), trace amounts (1–5%) of furan **8** and ketoaldehyde **11** were formed alongside of **6a** (see Scheme 2). Without added base, yields of **8** and **11** were much higher (ca. 20–40% each). A mechanistic rationale is depicted in Scheme 2: Compound **4a** is first converted into the intermediate peroxide **7**, which either undergoes fragmentation to **6a** via abstraction of H^a or, alternatively, elimination to furan **8** via abstraction of H^b. Furan **8** may then react to intermediate epoxide **9** which rearranges to ketoaldehyde **11**.[12] The amount and strength of base additive was critical for balancing the reaction and we applied K_3PO_4, Cs_2CO_3,[13] NaOAc and NaH_2PO_4 at 0.5–3.0 molar equivalents. However, among all parameters, temperature had the greatest impact on the yield of **6a**. Carrying out the reaction at 0 °C for 72 hours increased the yield by 10% compared to room temperature. Temperatures lower than 0 °C might further improve yield but reaction times and experimental inconvenience would increase accordingly. By the aforementioned measures, we could suppress the formation of **8** and **11** to a minimum but the major side reaction was still polymerization. Peroxide **7** may also undergo 1,4-elimination to furan-3(2*H*)-one **10**[13] and we could isolate this intermediate in one case (see below). This side reaction becomes increasingly dominant at elevated temperatures and enolizable compounds **10** are known to be very prone to polymerization.[14] Yet, we did not succeed in suppressing this undesired process satisfactorily, at least for substrates of type **4a**.



Scheme 2 Products formed in the TBHP oxidation of substrates **4** (see text). *Reagents and conditions*: a) $Mn(OAc)_3{\cdot}2H_2O$ (5 mol%), TBHP (5–6 equiv), base additive, O_2 atmosphere, 0 °C, 72 h.

We prepared a series of butenolides **6** and also γ-lactam **13** by our method and the results were similar for systems analogous to **4a** (Table 2, entries 2 and 3). A minor shift of the diastereomeric ratio was observed during preparation of lactone **6e**. Gratifyingly, reactions of spiro dihydrofurans **4g–i** proceeded more straightforward and lactones **6g–i** were isolated in good yields (entries 4–6). The transformation of **4i** required no base additive and butenolide **6i** was the sole product (73% yield). The analogous reaction of **4g** in turn gave **6g** in only 43% yield, along with 11% of the 1,4-elimination product (3-furanone), which was isolable in this case. Addition of carbonate base again improved the yield, up to 66% for **6g**. Remarkably, the presence of the electron-rich nitrogen is tolerated under these conditions as shown by the conversion **4h** → **6h**. The conversion of **12** into lactam **13** demonstrates that the reaction is also applicable to dihydropyrroles.

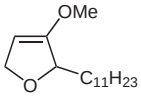
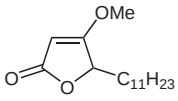
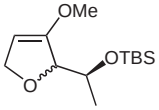
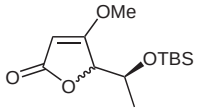
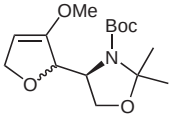
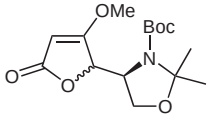
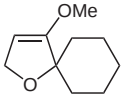
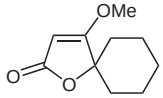
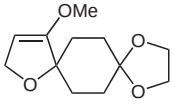
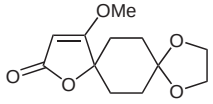
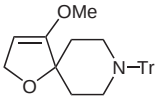
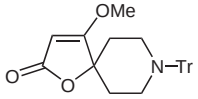
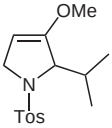
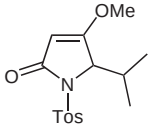
The utility of these findings was demonstrated by a short synthesis of the polyketide annularin H (**17**,[15a] Scheme 3). Commercially available methyl 3-oxovalerate (**14**) was converted into protected aldehyde **15** within three steps. Addition of lithiated methoxyallene and 5-*endo* cyclization with AuCl/pyridine provided dihydrofuran **16**, which upon allylic oxidation and deprotection furnished the racemic natural product **17**[17] with good overall efficiency.



Scheme 3 Preparation of (±)-annularin H (**17**). *Reagents and conditions*: a) 2,2-dimethylpropane-1,3-diol, $HC(OMe)_3$, amberlyst (H^+ form), CH_2Cl_2, r.t., overnight; b) $LiAlH_4$, Et_2O, 0 °C, 2 h; c) oxalyl chloride, DMSO, CH_2Cl_2, –60 °C to –40 °C, 30 min, then *i*-Pr_2NEt; d) methoxyallene (3.5 equiv), *n*-BuLi (3.0 equiv), Et_2O, –78 °C, 2.5 h; e) AuCl (5 mol%), pyridine (0.15 equiv), CH_2Cl_2, r.t., 1 h; f) $Mn(OAc)_3{\cdot}2H_2O$ (5 mol%), TBHP (5.0 equiv), Cs_2CO_3 (0.5 equiv), 4 Å MS, MeCN, O_2, 0 °C, 72 h; g) HCl aq, acetone, r.t., 22 h.

We will further investigate and improve the allylic and other oxidative transformations of alkoxyallene-based heterocycles. In fact, the protocols presented here should be useful for the synthesis of pyrrolidine alkaloids and iminosugars and our progress in these areas will be reported in due course.

Table 2 Oxidation of Dihydrofurans **4**[17] (Dihydropyrrole **12**) to Butenolides **6** (Lactam **13**)[a]

Entry	Substrate	Additive Cs_2CO_3 (equiv)	Conditions	Yield (%)	Product
1	**4a** 	0.50	0 °C, 72 h	46	**6a** 
2	**4d**  dr = 83:17	0.50	0 °C, 72 h	50	**6d**  dr = 85:15
3	**4e**  dr = 82:18	0.50	0 °C, 72 h	47	**6e**  dr = 73:27
4	**4i**[b] 	–	r.t., 48 h	73	**6i** 
5	**4g** 	– 0.50	r.t., 48 h r.t., 48 h	43 66	**6g** 
6	**4h** 	0.50	r.t., 48 h[c]	53	**6h** 
7	**12**[d] 	0.50	0 °C, 72 h	35	**13** 

[a] Conditions: $Mn(OAc)_3 \cdot 2H_2O$ (5 mol%), TBHP (5–6 equiv), 4 Å MS, O_2 atmosphere, MeCN.
[b] Compound prepared according to ref. 2b.
[c] Reaction carried out in CH_2Cl_2–MeCN (1:1).
[d] Compound prepared by cyclization of the parent allenyl amine with $AgNO_3$ and K_2CO_3.

Acknowledgment

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(16) **Typical Procedure for the Au(I)-Catalyzed Cyclization: Preparation of Compound 4g**
Methoxyallene (0.35 mL, 294 mg, 4.19 mmol) was dissolved in Et_2O (5 mL) at –40 °C. *n*-BuLi (1.40 mL, 2.5 M in hexane, 3.50 mmol) was added, the mixture was stirred for 20 min and then cooled to –78 °C. A solution of ketone **1g** (180 mg, 1.15 mmol) in Et_2O (2 mL) was slowly added and the mixture was stirred at –78 °C for 2.5 h. Then, H_2O (10 mL) was added and the mixture was warmed to r.t. The layers were separated and the aqueous layer was extracted with Et_2O (3×). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. Drying at 0.1 mbar provided the allenyl alcohol as a yellow oil (285 mg, quant.). The crude product (max. 1.15 mmol) was dissolved in CH_2Cl_2 (17 mL). Pyridine (15 μL, 15 mg, 190 μmol) and AuCl (13 mg, 56 μmol) were added with rapid stirring. After 1 h, TLC showed complete conversion. The mixture was concentrated in vacuo and directly chromatographed (silica gel, EtOAc–hexane = 1:3) to provide 222 mg (85% over 2 steps) of **4g** as a colorless solid. Analytical data for **4g**: mp 72–74 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.59–1.67, 1.86–1.91 (2 m, 2 × 4 H, 4 × CH_2), 3.61 (s, 3 H, OCH_3), 3.92 (m_c, 4 H, 2 × CH_2), 4.50 (t, *J* = 1.7 Hz, 1 H, 4-H), 4.52 (d, *J* = 1.7 Hz, 2 H, 5-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 30.7, 31.8 (2 t, 4 × CH_2), 57.4 (q, OCH_3), 64.1, 64.2 (2 t, 2 × CH_2), 70.2 (t, C-5), 82.5 (s, C-2), 88.2 (d, C-4), 108.3 [s, $C(OR)_2$], 161.4 (s, C-3) ppm. IR (KBr): ν = 2960–2850 cm^{-1} (=CH, CH). ESI-TOF: 249.1095 $[M + Na]^+$, 227.1277 $[M + H]^+$. Anal. Calcd for $C_{12}H_{18}O_4$ (226.3): C, 63.70; H, 8.02. Found: C, 63.47; H, 8.11.

(17) **Typical Procedure for the Allylic Oxidation: Preparation of (±)-Annularin H (17)**
Dihydrofuran **16** (520 mg, 2.03 mmol) was dissolved in MeCN (22 mL). Then, Cs_2CO_3 (335 mg, 1.03 mmol) and powdered 4 Å MS (1.02 g) were added. After cooling to 0 °C, TBHP (1.90 mL, 5.5 M solution in nonane, 10.5 mmol) and $Mn(OAc)_3 \cdot 2H_2O$ (27 mg, 101 μmol) were added and the flask was equipped with a balloon of O_2. The mixture was vigorously stirred at 0 °C for 72 h, then poured into an aqueous solution of $FeSO_4 \cdot 7H_2O$ (ca. 2.5 g in 30 mL H_2O), rinsing with EtOAc (10 mL). After 10 min of stirring, the mixture was filtered through Celite® with the aid of EtOAc (50 mL). The filtrate layers were separated and the aqueous layer was extracted with EtOAc (5×). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was dissolved in acetone–H_2O (8 mL/ 0.50 mL) and HCl (0.20 mL, 37% aq) was added. After 22 h of stirring at r.t., the mixture was poured into pH 7 phosphate buffer solution (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3×). The combined organic layers were dried ($MgSO_4$), filtered, concentrated, and chromatographed (silica gel, 100% EtOAc, R_f = 0.6) to provide 192 mg (51% over 2 steps) of **17** as a yellowish oil that solidified to a light yellow solid in the refrigerator. Analytical data for **17**: mp 55–57 °C (lit.[15] oil). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02 (t, *J* = 7.3 Hz, 3 H, CH_3), 2.46 (q, *J* = 7.3 Hz, 2 H, CH_2), 2.67 (dd, *J* = 8.5, 16.9 Hz, 1 H, 1′-H), 2.85 (dd, *J* = 3.6, 16.9 Hz, 1 H, 1′-H), 3.86 (s, 3 H, OCH_3), 5.05 (d, *J* = 1.0 Hz, 1 H, 3-H), 5.21 (ddd, *J* = 1.0, 3.6, 8.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 7.29 (q, CH_3), 36.7 (t, CH_2), 43.7 (t, C-1′), 59.5 (q, OCH_3), 74.4 (d, C-5), 88.7 (d, C-3), 171.8 (s, C-2), 181.8 (s, C-4), 206.1 (s, C-2′) ppm. Anal. Calcd for $C_9H_{12}O_4$ (184.2): C, 58.69; H, 6.57. Found: C, 58.25; H, 6.56. The analytical data are in agreement with those given in ref. 15.