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Gold(I)-catalyzed formation of furans by a Claisen-type rearrangement of ynenyl allyl ethers

Florin M. Istrate and Fabien Gagosz*

Abstract
A series of ynenyl allyl ethers were rearranged into polysubstituted furans in the presence of a gold(I) catalyst. It is proposed that the transformation involves a Claisen-type rearrangement that allows the efficient creation of quaternary centers under mild experimental conditions.

Findings
Furans represent an important class of heteroaromatic compounds, which are found in a large number of natural products, in synthetic biologically active substances and also in flavor chemicals [1,2]. Consequently, many efforts have been devoted to the development of synthetic methods which allow a rapid, efficient, and selective access to the furan motif [3-6]. Recently, several new strategies that involve a metal-mediated cyclization of an allene or an alkyne derivative with an oxygen functionality have appeared in the literature [7]. Among the transition metals that are commonly employed in these transformations (viz. Cu, Ag, Pd and Au), gold has proven to be particularly suitable given the strong 𝜋 Lewis acidic property of cationic gold species and their ability to activate alkenes and allenes towards the addition of oxygen functionalities [8-16].

The various alkynyl and allenyl compounds presented in Scheme 1 have thus proved to be suitable precursors for the formation of polysubstituted furans in the presence of a gold(I) or a gold(III) catalyst [17-44].

We report herein our own investigations in this field which have led to the development of a new procedure for the synthesis of polysubstituted furans by a gold-catalyzed cycloisomerization of ynenyl allyl ethers [45-48].

In the course of our work on the development of new gold-catalyzed transformations [49-51], we recently found that a series of ynenyl allyl tosylamides 1 (X = NTs) could be converted under mild experimental conditions into functional-
ized pyrroles 3 (X = NTs) in the presence of a gold(I) catalyst (Scheme 2) [52]. In contrast to Fürstner’s observations for the rearrangement of allyl pent-4-ynyl ethers [53,54], the results obtained during this study strongly suggested that no allyl cation was formed during the reaction. The substitution pattern of the pyrroles thus obtained point toward the involvement of a more concerted aza-Claisen-type rearrangement mechanism (2 → 3) and tend to exclude the possibility of a simple N to C allyl shift (2 → 4 → 5). Based on these initial findings, we envisaged that an analogous transformation could be employed for the synthesis of substituted furans 3 (X = O) from ynenyl allyl ethers 1 (X = O) (Scheme 2). The proof that a similar reaction can take place via an analogous pathway using oxygen- instead of nitrogen-derivatives would therefore support our initial mechanistic proposal and would broaden the scope of this new gold-catalyzed Claisen-type rearrangement [55-62].
Moreover this synthetic approach to furans would be particularly interesting for several reasons:

• The required ynenyl allyl ether substrates are easily accessible via various methods (see Supporting Information File 1 for more details),

• the Claisen-type rearrangement would allow the formation of two new C–O and C–C bonds in a single step,

• the reaction would allow the easy formation of quaternary centers and the introduction of a variety of other substituents on the side chain (when R4 ≠ H and R5 ≠ H),

• and the reaction could be particularly useful for the preparation of 2-butenylfurans, whose motif can be found in a variety of natural products, such as rubifolide [63], curzerene [64] or pumiloxide [65] (Figure 1).

Thus, a wide range of ynenyl allyl ethers 6a–s was synthesized (see Supporting Information File 1) and reacted under the conditions that were found to be optimal for the analogous formation of pyrroles from ynenyl allyl tosylamides, that is, 2 mol % of the gold catalyst [(p-CF3-C6H4)3P-Au-NTf2] [66] in dichloromethane at room temperature (Table 1).

Table 1: Scope of the gold(I)-catalyzed formation of furans.*

| entry | substrate | product | conversionb | yieldc |
|-------|-----------|---------|-------------|--------|
| 1     | 6a        | 7a      | 100%        | 18% (75%) |
| 2     | 6b      | 7b      | 100%        | 39% (86%) |
| 3     | 6c        | 7c      | 100%        | 59% (82%) |
| 4     | 6d        | 7d      | 100%        | 81% (92%) |

Figure 1: Natural products possessing a 2-butenylfuran motif.
Table 1: Scope of the gold(I)-catalyzed formation of furans. (continued)

| Entry | Starting Material | Product Structure | Product | Yield | Isolated Yield |
|-------|-------------------|-------------------|---------|-------|----------------|
| 5     | ![Structure 6e](image) | ![Structure 7e](image) | 7e      | 100%  | 66%            |
| 6     | ![Structure 6f](image) | ![Structure 7f](image) | 7f      | 100%  | 71%            |
| 7     | ![Structure 6g](image) | ![Structure 7g](image) | 7g      | 100%  | 63%            |
| 8     | ![Structure 6h](image) | ![Structure 7h](image) | 7h      | 100%  | quant.         |
| 9     | ![Structure 6i](image) | ![Structure 7i](image) | 7i      | 100%  | quant.         |
| 10    | ![Structure 6j](image) | ![Structure 7j](image) | 7j      | 100%  | 78%            |
| 11    | ![Structure 6k](image) | ![Structure 7k](image) | 7k      | 100%  | 78%            |
| 12    | ![Structure 6l](image) | ![Structure 7l](image) | 7l      | 100%  | 17%            |
Table 1: Scope of the gold(I)-catalyzed formation of furans.\(^a\) (continued)

| Entry | Structure 6 | Structure 7 | Conversion | Isolated Yield |
|-------|-------------|-------------|------------|----------------|
| 13    | ![Image](image1.png) | ![Image](image2.png) | 100%       | 77%            |
| 14    | ![Image](image3.png) | ![Image](image4.png) | 100%       | 80%            |
| 15    | ![Image](image5.png) | ![Image](image6.png) | 100%       | 90%            |
| 16    | ![Image](image7.png) | ![Image](image8.png) | 100%       | 82%            |
| 17    | ![Image](image9.png) | ![Image](image10.png) | 100%       | 86%            |
| 18    | ![Image](image11.png) | ![Image](image12.png) | >84%\(^g\) | 73%            |
| 19    | ![Image](image13.png) | ![Image](image14.png) | >62%\(^g\) | 36%            |

\(^a\)Reaction conditions: 0.1 M of substrate in DCM with 2 mol % of (p-CF\(_3\)-C\(_6\)H\(_4\))\(_3\)P-Au-NTf\(_2\) at rt for 10 minutes. \(^b\)Conversion of the substrate determined by \(^1\)H NMR of the crude mixture. \(^c\)Isolated yields. \(^d\)Yields determined by \(^1\)H NMR of the crude mixture (with 1,3,5-trimethoxybenzene as an internal reference). \(^e\)Z/E ratio = 1/3. \(^f\)Z/E ratio = 1/2.6. \(^g\)Reaction time: 40 minutes.

Under these conditions, we observed the rapid formation (usually less than 10 minutes) of the expected furans. The allyl (6a), crotyl (6b), prenyl (6c) and geranyl (6d) derivatives were readily cycloisomerized in the presence of the gold catalyst, but the isolation of the corresponding furans 7a–d proved to be quite challenging due to their high volatility (entries 1–4). These reactions were therefore performed in deuterated dichloromethane and their yields assessed by \(^1\)H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal reference (75–92%). All the examples presented in entries 2–19 are in
agreement with the postulated Claisen-type rearrangement since only the exclusive formation of branched products of type 3 was observed. Indeed, a linear product of type 5 resulting from an O to C shift of the allylic moiety could not be detected, whatever substrate was used [67]. Substrates 6b and 6e, which were used as a mixture of Z/E isomers, each afforded a single product, i.e., the furans 7b and 7e, respectively (entries 2 and 5). The cyclization of compounds 6f, 6g, 6o, 6q and 6s, which possess an exocyclic allylic moiety, furnished the corresponding furans 7f, 7g, 7o, 7q and 7s in moderate to quantitative yields (entries 6, 7, 15, 17 and 19). It is also worth noting that an increase in the substitution at the terminus of the allylic moieties of the substrates (monosubstitution in the case of 6b, disubstitution for 6c–s) did not notably influence the conversion, the rate or the yield of the reaction, even though the steric hindrance of the postulated Claisen intermediate 2 would have increased. This behavior strongly contrasts with the generally less efficient Claisen reactions of similarly substituted substrates and consequently allows the easy creation of a new quaternary center for the disubstituted substrates 6c–s (entries 3–19). Interestingly substrates 6h–m, which possess an extra substituent at the allylic position of the ynenyl fragment, also easily rearranged to afford the expected furans 7h–m in good to quantitative yields (entries 8–13). A large variety of substituents were tolerated including primary, secondary or tertiary alkyl groups and even a vinyl or a phenyl group. However, a poor yield (17%) was obtained when compound 6l was used as the substrate, due to the facile polymerization of the corresponding vinylfuran 7l (entry 12). Substituents other than a simple methyl group could be introduced at position C(3) of the furans. Substrates 6n–q, which possess either a phenyl or a longer alkyl chain, were indeed efficiently converted into compounds 7a–q (80–90%, entries 14–17). However, limited reactivity was observed with ethers 6r–s, which could not be completely converted into the corresponding furans 7r–s (entries 18–19).

A mechanistic proposal for the formation of furans 7a–s is presented in Scheme 3. It is based on the results shown in entries 2–19 (Table 1), which support the involvement of a gold-catalyzed Claisen-type rearrangement as the key step of the transformation.

The gold(I) activation of the alkyne moiety in substrate 6 could promote the nucleophilic addition of the oxygen atom, and lead to the formation of the cationic vinyl gold intermediate 8. A subsequent Claisen-type rearrangement would furnish the intermediate 9. The loss of a proton to allow aromatization of the system, followed by a protodemetalation step would finally give furan 7.

In summary, we have developed a new gold(I)-catalyzed formation of polysubstituted furans, which is characterized by its efficiency, the mild conditions employed and the easy formation of quaternary centers. The selectivity observed in the structure of the final product is in agreement with the postulated Claisen-type rearrangement. Further studies related to the development of an asymmetric version of this new gold(I)-catalyzed process and its application to the synthesis of natural products are underway.
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References
1. Keay, B. A.; Dibble, P. W. In Comprehensive Heterocyclic Chemistry II, A Review of the Literature 1982-1995; Katritzky, A. R.; Rees, C. W., Eds.; Pergamon Press: Oxford, 1997; Vol. 2, pp 395–436.
2. Donnelly, D. M. X.; Meegan, M. J. Furans and their Benzo Derivatives: (iii) Synthesis and Application. In Comprehensive Heterocyclic Chemistry; Katritzky, A. R.; Rees, C. W., Eds.; Pergamon Press: Oxford, 1994; Vol. 3, pp 657–712. doi:10.1016/B978-008096519-2.00062-X
3. Cacchi, S. J. Organomet. Chem. 1999, 576, 42–64. doi:10.1016/S0022-328X(98)01051-1
4. Keay, B. A. Chem. Soc. Rev. 1999, 28, 209–215. doi:10.1039/a904839j
5. Hou, L.; Cheung, H. Y.; Hon, T. Y.; Kwan, P. L.; Lo, T. H.; Tong, S. Y.; Wong, H. N. C. Tetrahedron 1998, 54, 1955–2020. doi:10.1016/S0040-4020(97)10303-9
6. König, B. Heterocycles and Related Ring Systems: Fully Unsaturated Small-Ring Heterocycles and Monocyclic Five-Membered Heterocycles with One Heteroatom. In Houben-Weyl, Methoden der organischen Chemie, 4th ed.; Thieme: Stuttgart, Germany, 2001; Vol. 9, pp 183–286.
7. Brown, R. C. D. Angew. Chem., Int. Ed. 2005, 44, 850–852. doi:10.1002/anie.200461668
8. Fürstner, A. Chem. Soc. Rev. 2009, 38, 3208–3221. doi:10.1039/b816696j
9. Michelet, V.; Toulec, P. Y.; Genêt, J. P. Angew. Chem., Int. Ed. 2008, 47, 4286–4315. doi:10.1002/anie.200701589
10. Jiménez-Núñez, E.; Echavarren, A. M. Chem. Rev. 2008, 108, 3326–3350. doi:10.1021/cr0804319
11. Li, Z.; Brower, C.; He, C. Chem. Rev. 2008, 108, 3239–3265. doi:10.1021/cr0804341
12. Arcadi, A. Chem. Rev. 2008, 108, 3266–3325. doi:10.1021/cr080435d
13. Gorin, D. J.; Sherry, B. D.; Toste, F. D. Chem. Rev. 2008, 108, 3351–3378. doi:10.1021/cr080430g
14. Muzart, J. Tetrahedron 2008, 64, 5815–5849. doi:10.1016/j.tet.2008.04.018
15. Hashmi, A. S. K. Chem. Rev. 2007, 107, 3180–3211. doi:10.1021/cr060436x
16. Fürstner, A.; Davies, P. W. Angew. Chem., Int. Ed. 2007, 46, 3410–3449. doi:10.1002/anie.200604335
17. Zhang, J.; Schmalz, H.-G. Angew. Chem., Int. Ed. 2006, 45, 6704–6707. doi:10.1002/anie.200601252
18. Suhre, M. H.; Reif, M.; Kirsch, S. F. Org. Lett. 2007, 9, 3925–3927. doi:10.1021/o10514101
19. Praveen, C.; Kirthiga, P.; Perumal, P. T. Synlett 2009, 1990–1996. doi:10.1055/s-0029-1217517
20. Kim, S.; Kang, D.; Shin, S.; Lee, P. H. Tetrahedron Lett. 2010, 51, 1899–1901. doi:10.1016/j.tetlet.2010.02.026
21. Hashmi, A. S. K.; Schwarz, L.; Choi, J.-H.; Frost, T. M. Angew. Chem., Int. Ed. 2000, 39, 2285–2288. doi:10.1002/1521-3773(20000703)39:13<2285::AID-ANIE2285>3.0.CO;2-F
22. Dudnik, A. S.; Xia, Y.; Li, Y.; Georgy and, V. J. Am. Chem. Soc. 2010, 132, 7645–7655. doi:10.1021/ja910290c
23. Zhou, C.-Y.; Chan, P. W. H.; Che, C.-M. Org. Lett. 2006, 8, 325–328. doi:10.1021/ol050269c
24. Ji, K.-G.; Shu, X.-Z.; Chen, J.; Zhao, S.-C.; Zheng, Z.-J.; Liu, X.-Y.; Liang, Y.-M. Org. Biomol. Chem. 2009, 7, 2501–2505. doi:10.1039/b905332h
25. Shu, X.-Z.; Liu, X.-Y.; Xiao, H.-Q.; Ji, K.-G.; Guo, L.-N.; Qi, C.-Z.; Liang, Y.-M. Adv. Synth. Catal. 2007, 349, 2493–2498. doi:10.1002/adsc.200700319
26. Yao, T.; Zhang, X.; Larock, R. C. J. Org. Chem. 2005, 70, 7679–7685. doi:10.1021/jo051058s
27. Yao, T.; Zhang, X.; Larock, R. C. J. Am. Chem. Soc. 2004, 126, 11164–11165. doi:10.1021/ja0466694
28. Kramer, S.; Madsen, J. L. H.; Röttländer, M.; Skrydstrup, T. Org. Lett. 2010, 12, 2758–2761. doi:10.1021/ol100868s
29. Hashmi, A. S. K.; Sinha, P. Adv. Synth. Catal. 2004, 346, 432–438. doi:10.1002/adsc.200303201
30. Blanc, A.; Alix, A.; Weibel, J.-M.; Pale, P. Eur. J. Org. Chem. 2010, 1644–1647. doi:10.1002/ejoc.200901331
31. Blanc, A.; Tenbrink, K.; Weibel, J.-M.; Pale, P. J. Org. Chem. 2009, 74, 5342–5348. doi:10.1021/jo9008172
32. Liu, Y.; Song, F.; Song, Z.; Liu, M.; Yan, B. Org. Lett. 2005, 7, 5409–5412. doi:10.1021/ol052160p
33. Du, X.; Song, F.; Lu, Y.; Chen, H.; Liu, Y. Tetrahedron 2009, 65, 1839–1845. doi:10.1016/j.tet.2008.11.109
34. Zhang, X.; Lu, Z.; Fu, C.; Ma, S. J. Org. Chem. 2010, 75, 2569–2598. doi:10.1021/jo101465p
35. Belling, V.; Krause, N. Org. Biomol. Chem. 2009, 7, 1221–1225. doi:10.1039/b819704k
36. Aponick, A.; Li, C.-Y.; Malinge, J.; Marques, E. F. Org. Lett. 2009, 11, 4624–4627. doi:10.1021/ol9001901
37. Egi, M.; Azechi, K.; Akai, S. Org. Lett. 2009, 11, 5002–5005. doi:10.1021/ol901942t
38. Marshall, J. A.; Robinson, E. D. J. Org. Chem. 1999, 52, 1495–1498. doi:10.1021/jo00298a012
39. Marshall, J. A.; Sehon, C. A. J. Org. Chem. 1995, 60, 5966–5968. doi:10.1021/jo0023a040
40. Schwier, T.; Sromek, A. W.; Yap, D. M. L.; Chernyak, D.; Gevorgyan, V. J. Am. Chem. Soc. 2007, 129, 9668–9878. doi:10.1021/ja072446m
41. Yazici, A.; Pyne, S. G. Tetrahedron Lett. 2011, 52, 1396–1400. doi:10.1016/j.tetlet.2011.01.120
42. Hashmi, A. S. K. Angew. Chem., Int. Ed. Eng. 1995, 34, 1581–1583. doi:10.1002/anie.199515811
43. Ma, S. M.; Zhang, J. L.; Lu, L. Chem.–Eur. J. 2003, 9, 2447–2456. doi:10.1002/chem.200204664
44. Fukuda, Y.; Shiragami, H.; Utimoto, K.; Nozaki, H. J. Org. Chem. 1991, 56, 5816–5819. doi:10.1021/jo00020a024
45. Gabriele, B.; Salerno, G.; Lauria, E. J. Org. Chem. 1999, 64, 7687–7692. doi:10.1021/jo990847h
46. Gabriele, B.; Salerno, G.; De Pascali, F.; Costa, M.; Chiussi, G. P. J. Org. Chem. 1999, 64, 7693–7699. doi:10.1021/jo990848+
47. Gabriele, B.; Salerno, G. Chem. Commun. 1997, 1083–1084. doi:10.1039/a701988b
48. Gabriele, B.; Salerno, G.; De Pascali, F.; Scianò, G. T.; Costa, M.; Chiussi, G. P. Tetrahedron Lett. 1997, 38, 6877–6880. doi:10.1016/S0040-4039(97)01584-0
49. Bolte, B.; Odabachian, Y.; Gagosz, F. J. Am. Chem. Soc. 2010, 132, 7294–7296. doi:10.1021/ja1020469
50. Dias Jurberg, I.; Odabachian, Y.; Gagosz, F. J. Am. Chem. Soc. 2010, 132, 3543–3552. doi:10.1021/ja9100134
51. Gronnier, C.; Odabachian, Y.; Gagosz, F. Chem. Commun. 2011, 47, 218–220. doi:10.1039/c0cc00033g
52. Istrate, F. M.; Gagosz, F. Org. Lett. 2007, 9, 3181–3184. doi:10.1021/ol0713032
53. Fürstner, A.; Stelzer, F.; Szillat, H. J. Am. Chem. Soc. 2001, 123, 11863–11869. doi:10.1021/ja0109343
54. Fürstner, A.; Szillat, H.; Stelzer, F. J. Am. Chem. Soc. 2000, 122, 6785–6786. doi:10.1021/ja001034+
55. Saito, A.; Konishi, T.; Hanzawa, Y. Org. Lett. 2010, 12, 372–374. doi:10.1021/ol902716n
56. Bae, H. J.; An, S. E.; Cheong, J. Y.; Rhee, Y. H.; Duschek, A.; Kirsch, S. F. Org. Lett. 2008, 10, 2605–2607. doi:10.1021/ol8008733
57. Sherry, B. D.; Toste, F. D. J. Am. Chem. Soc. 2004, 126, 15978–15979. doi:10.1021/ja044602k
58. Williams, D.; Andersen, R. J.; Van Duyne, G. D.; Clardy, J. J. Org. Chem. 1987, 52, 332–335. doi:10.1021/jo00379a002
59. Williams, D.; Andersen, R. J.; Van Duyne, G. D.; Clardy, J. J. Org. Chem. 1987, 52, 332–335. doi:10.1021/jo00379a002
60. Williams, D.; Andersen, R. J.; Van Duyne, G. D.; Clardy, J. J. Org. Chem. 1987, 52, 332–335. doi:10.1021/jo00379a002
61. Williams, D.; Andersen, R. J.; Van Duyne, G. D.; Clardy, J. J. Org. Chem. 1987, 52, 332–335. doi:10.1021/jo00379a002
62. Williams, D.; Andersen, R. J.; Van Duyne, G. D.; Clardy, J. J. Org. Chem. 1987, 52, 332–335. doi:10.1021/jo00379a002
63. Williams, D.; Andersen, R. J.; Van Duyne, G. D.; Clardy, J. J. Org. Chem. 1987, 52, 332–335. doi:10.1021/jo00379a002
64. Williams, D.; Andersen, R. J.; Van Duyne, G. D.; Clardy, J. J. Org. Chem. 1987, 52, 332–335. doi:10.1021/jo00379a002
65. Williams, D.; Andersen, R. J.; Van Duyne, G. D.; Clardy, J. J. Org. Chem. 1987, 52, 332–335. doi:10.1021/jo00379a002
66. Williams, D.; Andersen, R. J.; Van Duyne, G. D.; Clardy, J. J. Org. Chem. 1987, 52, 332–335. doi:10.1021/jo00379a002
67. Within the limits of detection by 1H NMR spectroscopy of the crude reaction mixture.

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