Pergamon

Tetrahedron Letters 40 (1999) 989–990

TETRAHEDRON
LETTERS

# A new regioselective synthesis of 3-substituted furan-2(5*H*)-ones by palladium-catalysed reductive carbonylation of alk-1-ynes

Bartolo Gabriele,[a] Giuseppe Salerno,[a] Mirco Costa [b] and Gian Paolo Chiusoli [b]

[a] *Dipartimento di Chimica, Università della Calabria, 87030 Arcavacata di Rende, Cosenza, Italy*

[b] *Dipartimento di Chimica Organica e Industriale, Università di Parma, Viale delle Scienze, 43100 Parma, Italy*

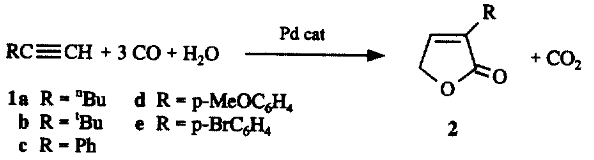
Received 30 September 1998; accepted 17 November 1998

**Abstract:** 3-Alkyl- or 3-aryl-substituted furan-2(5*H*)-ones are obtained directly in fair yields by reductive carbonylation of alk-1-ynes in the presence of catalytic amounts of palladium iodide in conjunction with potassium iodide (10 eq.) and water (200 eq.). Simultaneous oxidation of CO to $CO_2$ accounts for the stoichiometry of the process. Reactions are carried out in dioxane under mild conditions (80 °C and 10 atm of carbon monoxide).

Keywords: *alkynes; carbonylation; furanones; palladium*

We recently reported the combined oxidative and reductive carbonylation of alk-1-ynes catalysed by $PdI_2$ in the presence of thiourea as the ligand.[1] Reactions were carried out in methanol at room temperature and under an atmospheric pressure of carbon monoxide and afforded a mixture of maleic diesters (from oxidative carbonylation) and furan-2(5*H*)-ones (from reductive carbonylation) as the main products in a *ca.* 1:1 ratio. When applied to substrates containing a potentially reducible group, this method allowed the selective synthesis of a single product resulting from the combination of oxidative carbonylation and reduction within the same molecule.[2]

Now we wish to report a new method for the selective synthesis of 3-alkyl- or 3-aryl-substituted furan-2(5*H*)-ones by palladium-catalysed reductive carbonylation of alk-1-ynes in the presence of water. The reductive carbonylation occurs in conjunction with the oxidation of CO to $CO_2$, so the overall process corresponds to that represented in eqn. (1).



(1)

*PII:* S0040-4039(98)02464-2

In a typical experiment, a 300 ml stainless steel autoclave was charged with $PdI_2$ (36 mg, 0.1 mmol), KI (166 mg, 1 mmol), a solution of the alkyne **1** (10 mmol) in dry dioxane (20 ml) and $H_2O$ (360 μL, 20 mmol). The autoclave was purged several times with CO, then charged with CO (10 atm) and eventually heated at 80 °C with stirring for 15 h. After the usual work-up, the reaction crude was analysed by GLC and products were isolated by column chromatography ($SiO_2$) using appropriate hexane-ethyl acetate mixtures as eluent.

The results obtained with different alk-1-ynes are reported in the Table. Unidentified heavy products were present in the reaction mixtures deriving from arylacetylenes and accounted for the substrate conversion.

**Table** Reactions of alk-1-ynes (100 eq) with CO (10 atm) and $H_2O$ (200 eq) in dry dioxane in the presence of $PdI_2$ (1 eq) and KI (10 eq), substrate conc.: 0.5 mmol/mL dioxane, T = 80 °C, t = 15 h

| Run | Substrate | Conv'n (%) [a] | Yield of **2** (%) [b] | Total yield (%) [c] |
|---|---|---|---|---|
| 1 | **1a** | 98 | 77 (65) | 95 [d] |
| 2 | **1b** | 81 | 60 (51) | 68 [e] |
| 3 | **1c** | 100 | 67 (60) | 67 |
| 4 | **1d** | 100 | 65 (59) | 65 |
| 5 | **1e** | 100 | 51 (45) | 51 |

[a] Based on starting alk-1-yne, by GLC. [b] GLC yield (isolated yield). [c] By GLC; unidentified heavy products are not included. [d] Including 4-$^{n}$butyl-2(5*H*)furan-2-one (8%), 3-$^{n}$butylmaleic anhydride (7%) and 3-$^{n}$butylsuccinic anhydride (3%). [e] Including 3-$^{t}$butylmaleic anhydride (8%).

It is noteworthy that the reaction is very regioselective, the 3-substituted furan-2(5*H*)-one being obtained as the most abundant isomer in all cases. For simple *n*-alkylacetylenes such as hex-1-yne **1a** the ratio between the 3-substituted furan-2(5*H*)-one and the 4-substituted one was about 11 (run 1), while for $^{t}$butylacetylene **1b** and arylacetylenes **1c-e** the 3-substituted isomer was formed exclusively (runs 2-5).

The presence of water is essential to the process, only traces of product being obtained under anhydrous conditions. The use of $PdCl_2$ +10 KCl afforded only traces of oxidative carbonylation products (maleic anhydrides) without any formation of furanones **2**.

This is the first example of palladium-catalysed reductive carbonylation of alkynes to furan-2-(5*H*)-ones. A recently reported method for the synthesis of furan-2(5*H*)-ones from alkynes under water-gas shift conditions, requiring 100 atm of carbon monoxide, employed rhodium(0)carbonyl clusters as the catalytic system and always afforded mixtures of isomeric 3- and 4-substituted furanones in comparable amounts.[3]

## REFERENCES

1. Gabriele, B.; Salerno, G.; Costa, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1995**, 503, 21-28.
2. (a) Bonardi, A.; Costa, M.; Gabriele, B.; Salerno, G.; Chiusoli, G. P. *J. Chem. Soc., Chem. Commun.* **1994**, 2429-2430; (b) Costa, M.; De Souza Santos, L.; Chiusoli, G. P.; Gabriele, B.; Salerno, G. *J. Mol. Catal.* **1993**, *78*, 151-158.
3. Joh, T.; Nagata, H.; Takahashi, S. *Inorg. Chim. Acta* **1994**, *220*, 45-53.