



Tetrahedron report 1096

Base-free palladium-mediated cycloalkenylations of olefinic enolic systems



Jean Le Bras, Jacques Muzart*

Institut de Chimie Moléculaire de Reims, UMR 7312, CNRS–Université de Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cedex 2, France

ARTICLE INFO

Article history:

Received 9 July 2015

Available online 21 October 2015

Keywords:

Cycloalkenylation

Palladium

Enols

Mechanism

Contents

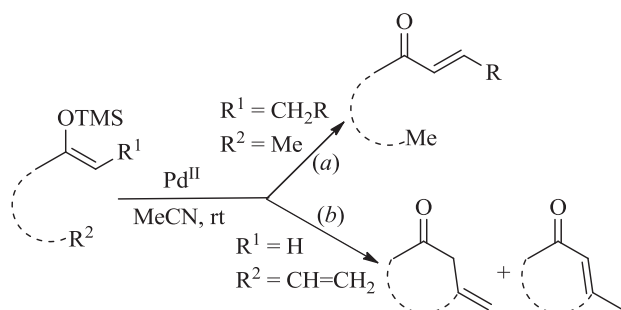
1. Introduction	9036
2. Olefinic enol silyl ethers	9036
2.1. Acyclic enol silyl ether unit, reactivity	9036
2.2. Cyclic enol silyl ether unit, reactivity	9037
2.2.1. 2-(Alk-3(or 4)-en-1-yl)-1-silyloxycyclohex-1-enes	9037
2.2.2. 3-(Alk-3(or 4)-en-1-yl)-1-silyloxycycloalk-1-enes	9038
2.2.3. 4-(Alk-2(or 3)-en-1-yl)-1-silyloxycycloalk-1-enes	9039
2.2.4. 5-(Alk-2(or 3)-en-1-yl)-2-silyloxycyclohexa-1,3-dienes	9040
2.2.5. 5-Trimethylsilyloxy-7a-allyl-2,6,7,7a-tetrahydro-1H-indene	9042
2.2.6. 3-(Alk-3-en-1-yl)-2-silyloxycycloalk-1-enes	9042
2.2.7. 1,5-Diallenyl-2-silyloxycyclohexa-1,3-dienes	9043
2.2.8. 1-Silyloxycycloalka-1,5(or 6)-dienes	9044
2.3. Mechanisms	9044
2.3.1. Saegusa's mechanism	9044
2.3.2. Kende's mechanism	9044
2.3.3. Favor and disfavor points, selectivity	9044
3. Olefinic silyl ketene acetals	9048
3.1. Reactivity	9048
3.2. Mechanism	9048
4. Olefinic methyl enol ethers	9048
4.1. Reactivity	9048
4.2. Mechanism	9049
5. Olefinic β -diketones	9049
5.1. Reactivity	9049
5.2. Mechanism	9050
6. Olefinic β -keto esters	9050
6.1. ξ -Alkenyl- β -keto esters	9050
6.2. Alkenyl-2-(methylcarboxy)cycloalka(or e)nonones	9051
6.3. Mechanisms	9052

* Corresponding author. E-mail address: jacques.muzart@univ-reims.fr (J. Muzart).

7.	Olefinic β -lactone esters	9052
7.1.	Reactivity	9052
7.2.	Mechanism	9053
8.	Olefinic β -keto amides	9053
8.1.	Reactivity	9053
8.2.	Mechanism	9054
9.	Olefinic β -amide or lactam esters	9055
9.1.	Reactivity	9055
9.2.	Mechanism	9056
10.	Olefinic α -cyano ketones	9056
10.1.	Reactivity	9056
10.2.	Mechanism	9057
11.	Conclusion	9057
	References and notes	9058
	Biographical sketch	9059

1. Introduction

In 1978, Saegusa and co-workers disclosed the synthesis of α,β -unsaturated ketones from the Pd^{II} -promoted oxidative dehydrogenation of trimethylsilyl enol ethers (Scheme 1, path a).¹ One year later, Saegusa's team reported that same experimental conditions can mediate a ring construction when the substrate bears an olefinic tether.² This cyclization involves the formation of a C–C bond between the C-extremity of the enolic moiety and one carbon of the C=C unit (Scheme 1, path b).



Scheme 1. Oxidative dehydrogenation versus cycloalkenylation of trimethylsilyl enol ethers.

Subsequently, other teams reported that Pd^{II} promotes the base-free cyclization of various olefinic functionalized substrates able to produce enolic species. These cycloalkenylation procedures have been exploited for the production of a number of unsaturated carbonyl compounds, some of them having a bridged or spirannic polycyclic skeleton and being intermediates of the multiple step synthesis of natural products.^{3,4,5,6,7}

The present review covers these different Pd -mediated cycloalkenylations in highlighting the factors-depending selectivities and mechanisms, and mentioning their applications in synthesis. This review is organized by the type of substrate with, mainly, a chronological account of the reports.

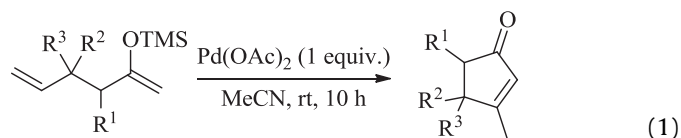
2. Olefinic enol silyl ethers

The crude olefinic silyl ether is sometimes used for the cycloalkenylation reaction. As the corresponding literature only reports the overall yield of the two steps, i.e., silylation and then cyclization,

both steps are mentioned into the corresponding equations, but experimental conditions are only disclosed for the cyclization.

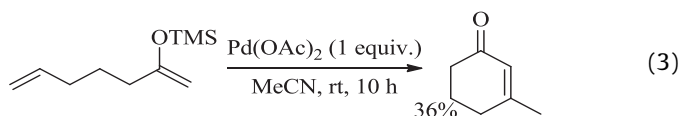
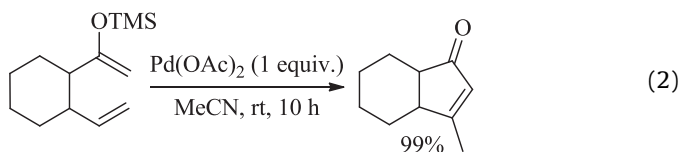
2.1. Acyclic enol silyl ether unit, reactivity

The typical Saegusa cycloalkenylation procedure uses olefinic trimethylsilyl ethers and a stoichiometric amount of $\text{Pd}(\text{OAc})_2$ in acetonitrile at room temperature.² A variety of cycloalkenones was thus obtained in yields depending on the size of the ring (Eqs. 1–4). The efficiency also depends on the substitution of the C=C bond (Eq. 5): while the cycloalkenylation of the trimethylsilyl derivative of hept-5-en-2-one occurred in 60% yield, that of 6-methylhept-5-en-2-one derivative was ineffective; switching to $\text{PdCl}_2(\text{PhCN})_2$ in benzene as experimental conditions improved this cycloalkenylation. The synthesis in MeCN of 3-methyl-2-cyclopentenone with substoichiometric amounts of $\text{Pd}(\text{OAc})_2$ associated to reoxidants has been tested: lower yields were obtained with benzoquinone, even in the presence of 0.5 equiv of the catalyst (Eq. 1), while $\text{Cu}(\text{OAc})_2/\text{O}_2$ combinations were unsuccessful.²



$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$: 87% (70%^a); $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{R}^3 = \text{H}$: 98%
 $\text{R}^1 = \text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$: 83%; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{Me}$: 100%

^aWith 0.5 equiv. of both $\text{Pd}(\text{OAc})_2$ and benzoquinone



Download English Version:

<https://daneshyari.com/en/article/5214315>

Download Persian Version:

<https://daneshyari.com/article/5214315>

[Daneshyari.com](https://daneshyari.com)