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Base-free palladium-mediated cycloalkenylations of olefinic enolic systems

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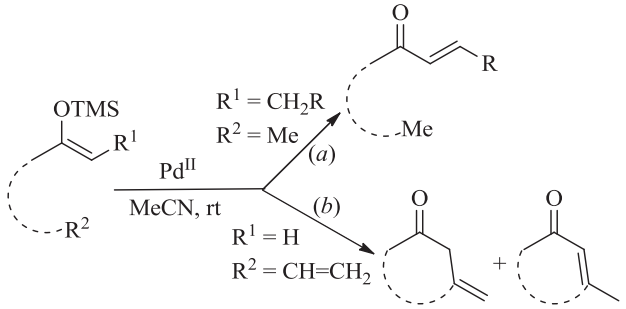
1. Introduction

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]

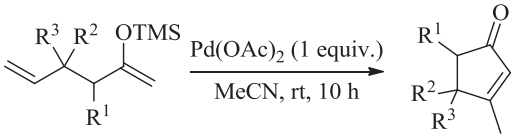
The present review covers these different Pd-mediated cycloakenylations in highlighting the factors-depending selectivities and mechanisms, and mentioning their applications in synthesis. This review is organized by the type of substrate with, mainly, a chronological account of the reports.

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.

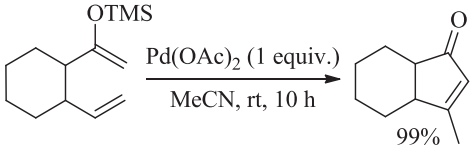
2.1. Acyclic enol silyl ether unit, reactivity

The typical Saegusa cycloalkenylation procedure uses olefinic trimethylsilyl ethers and a stoichiometric amount of $Pd(OAc)_2$ 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 $PdCl_2(PhCN)_2$ in benzene as experimental conditions improved this cycloalkenylation. The synthesis in MeCN of 3-methyl-2-cyclopentenone with substoichiometric amounts of $Pd(OAc)_2$ 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 $Cu(OAc)_2/O_2$ combinations were unsuccessful.[2]

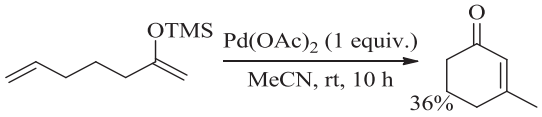


(1)

$R^1 = R^2 = R^3 = H$: 87% (70%[a]); R^1 = Me, $R^2 = R^3 = H$: 98%
$R^1 = R^2 = H$, R^3 = Ph: 83%; $R^1 = H$, $R^2 = R^3$ = Me: 100%
[a]With 0.5 equiv. of both $Pd(OAc)_2$ and benzoquinone



(2)



(3)