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PALLADIUM-CATALYZED RING EXPANSION OF VINYL OXASPIROHEXANES

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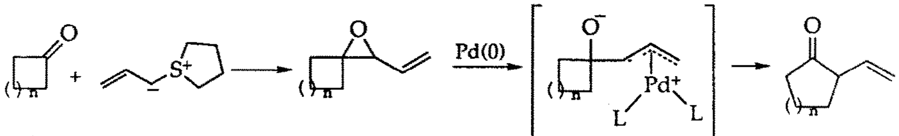
Abstract : *Pd(0)-catalyzed ring expansion of vinyl oxaspirohexanes occurred smoothly in the presence of 1 equiv of p-nitrophenol in tetrahydrofuran, yielding initially 2-vinylcyclopentanones in high yields. However, vinyl oxaspiroheptanes failed to undergo ring expansion under the present conditions.*

Palladium mediated reaction of vinyl epoxides has attracted a great deal of attention in recent years.[1] Our interest in the ring expansion of cycloalkanones[2] led us to examine the possibility of whether π-allylpalladium cationic species **4** would rearrange to give the ring-expanded cycloalkanones **5**.[3]



1 **2** **3** **4** **5**

Vinyl epoxides **3** were prepared by the reaction of cycloalkanones with allyl sulfur ylide **2** derived from allyl sulfonium salt.[4] Reaction of the vinyl epoxide **6** with 5 mol% Pd[PPh_3]$_4$ in tetrahydrofuran at room temperature for 3 h afforded the cyclopentanone **7** in 10% yield along with the byproduct **8** in 60% yield as a major product. Apparently, it was produced from nucleophilic attack of the enolate, derived from proton abstraction of the ring-expanded product by an alkoxy anion of π–allyl Pd species, to the π–allyl Pd species. Thus, it was required to quench a tertiary alkoxy anion somehow prior to proton abstraction by an alkoxy anion. In order to protonate an alkoxy anion, sterically bulky phenols, triphenylcarbinol and pyridinium *p*-toluenesulfonate were added but no major improvements were made. In the presence of acetic acid, the vinyl epoxide **6** afforded exclusively a 1:1 regioisomeric mixture of **9** and **10** in 87% yield, indicating that nucleophilic substitution is much faster than ring expansion. Pd(0)-catalyzed ring expansion of **9** and **10** was very slow, requiring 3 days in refluxing tetrahydrofuran to give 2-ethylidenecyclopentanone **7** in 88% yield. It was found that p-nitrophenol was much more effective as an additive and ring expansion was complete within 1 h in refluxing tetrahydrofuran.[5]

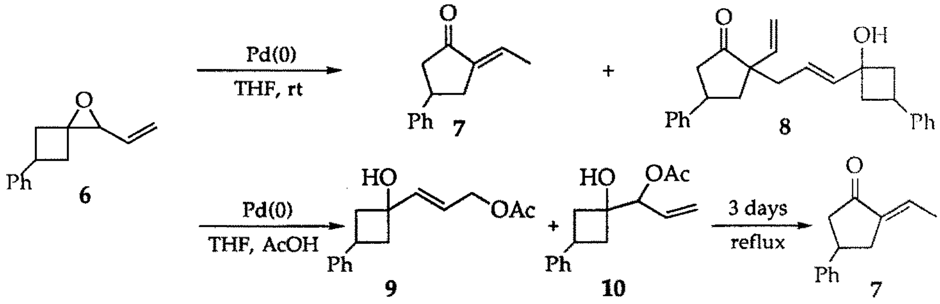
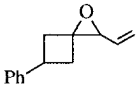
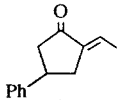
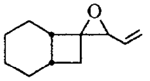
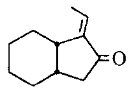
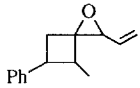
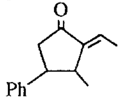
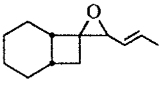
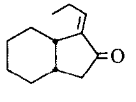
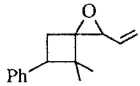
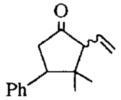
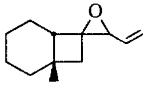
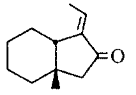
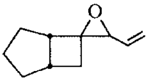
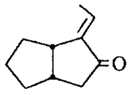
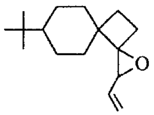
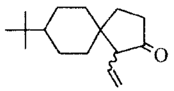


Table 1. Pd(0)-catalyzed ring expansion of vinyl oxaspirohexanes[a]

substrate	condition	product	yield, %	substrate	condition	product	yield, %
	reflux, 1.0 h		83		r.t, 2.0 h		81
	r.t, 3.0 h		85		reflux, 3.0 h		90
	r.t, 0.2 h		88		r.t, 2.5 h		73
	r.t, 2.0 h		90		r.t, 0.2 h		87

[a] The reaction was carried out with 5 mol% $Pd[PPh_3]_4$ in the presence of 1 equiv of *p*-nitrophenol in THF.

Some of our experimental results are shown in Table 1. Under the present conditions, vinyl oxaspirohexanes underwent facile ring expansion to yield 2-ethylidenecyclopentanones in high yields.When the migrating group was secondary alkyl group, the reaction occurred at room temperature. In the case of a tertiary migrating group, the reaction was complete almost instantly, yielding 2-vinylcyclopentanones without the isomerization of the double bond. Furthermore, the presence of vinyl methyl was expected to stabilize π–allyl Pd complex. Indeed, the reaction became slow and required heating for 3h.

It is noteworthy that vinyl oxaspiroheptanes failed to undergo ring expansion under the present conditions. In the presence of acetic acid, only the corresponding allylic acetates were obtained and no further reaction occurred, even after prolonged heating. The similar result was obtained in the presence of *p*-nitrophenol.

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