

A PALLADIUM-CATALYZED REARRANGEMENT OF 1-VINYL-1-CYCLOBUTANOLS

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Abstract: 2-methyl-2-cyclopentene-1-ones are produced by treating 1-vinyl-1-cyclobutanols with bis(benzonitrile)palladium dichloride and benzoquinone in THF.

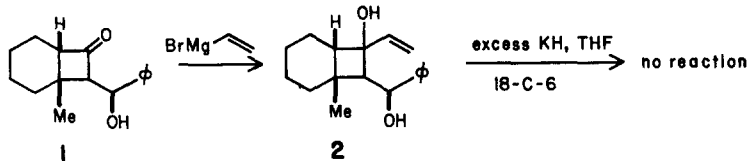
The vinylcyclobutane rearrangement is a cyclohexannulation which needs an olefin as the ultimate starting material. Danheiser,¹ Cohen,^{3,4} and others⁴ have studied the rearrangement for the purpose of learning its scope and limitations. Basically, those workers studied the rearrangements of 1-vinyl-2-cyclobutanols. The anion-accelerated version of the rearrangement was reported to be useful with this substitution pattern.^{1,2,3} The particular implementation involved treating the alcohol with potassium hydride in tetrahydrofuran with or without 18-crown-6 added,^{2,3} or by adding methyllithium to the product of cyclobutanone reduction by a trialkyl borohydride.¹ In the single reported attempt at the rearrangement of a 1-vinyl-1-cyclobutanol, it was reported that black tars were produced.⁵

Sano, Tsuda *et al.* have reported the vinylcyclobutane rearrangement of 1-vinyl-1-cyclobutanol silyl ethers in the presence of fluoride ion.^{6,7} Thus, the previous failure with this substitution pattern might be ascribed to insufficient ion pair separation with the potassium hydride/18-crown-6 protocol. Cyclobutanones are readily made by known routes⁸⁻¹² and may be further functionalized through the recently-reported aldol reaction of a cyclobutanone enolate with aldehydes.¹³ We were interested in determining whether these substrates could effectively undergo further conversions to other useful synthesis intermediates through rearrangement, for instance.

The cyclobutanone aldol **1**¹³ was exposed¹⁴ to vinylmagnesium bromide to give the vinylcyclobutanol **2**. This was treated with potassium hydride and 18-crown-6 and was inert to extended reflux in THF or DME. We were aware of the Japanese work cited above,^{6,7} but felt that silylation of the tertiary allylic alcohol would not be a trivial matter. We therefore sought another means of catalyzing the rearrangement of the

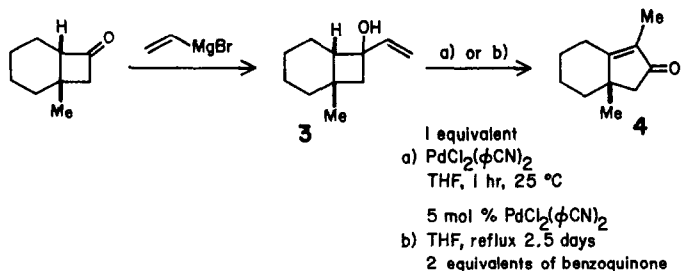
1-vinyl-1-cyclobutanols.

Scheme 1



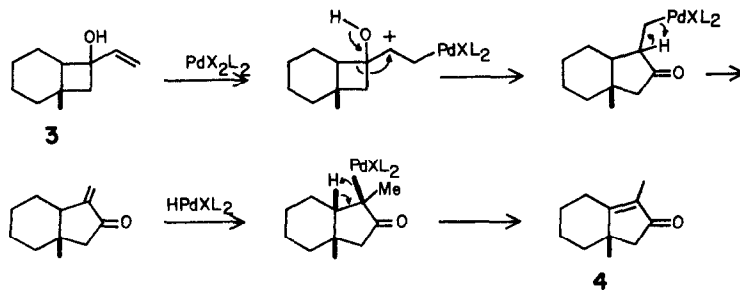
We now report that 1-vinyl-1-cyclobutanols, readily undergo ring expansion to give 2-methyl-2-cyclopentene-1-ones in the presence of bis(benzonitrile)palladium dichloride.¹⁵⁻¹⁷ Initial studies focussed on defining conditions that would lead to product formation. As an example, we were particularly pleased when the exposure of the 1-vinyl-1-cyclobutanol 3 to a full equivalent of bis(benzonitrile)palladium dichloride¹⁸ in THF quickly and smoothly gave a reaction product. Spectroscopic characterization indicated it to be the cyclopentenone 4.¹⁹

Scheme 2

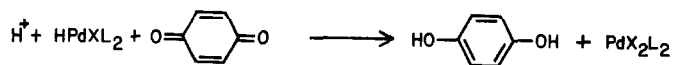


We desired to carry out the reaction using a catalytic amount of palladium. After many hours of reflux with the palladium complex, the reaction mixture turns black, and further reaction ceases. We believe that to be due to the formation of metallic palladium. However, when benzoquinone (2 equivalents) is added, the reaction proceeds smoothly albeit somewhat slowly in refluxing THF to give the desired cyclopentenone. The sequence of steps indicated in Scheme 3 is a plausible mechanistic pathway.

Scheme 3

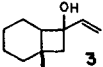
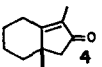
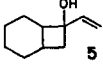
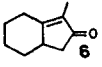
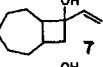
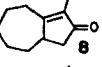
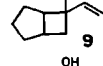
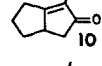
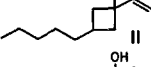
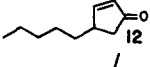







Scheme 3 (continued)



The results of a modest study are reported in the Table below. The ready formation of the fused 5,5 5,6 and 5,7 ring systems is notable. The variation in yield with phenyl as a substituent is not understood at this time. Finally, the last entry provides a potential building block for prostaglandin synthesis.

Although the rearrangements in entries 1-6 require an extended period of reflux for consumption of the starting material, the reaction in entry 7 occurs within 2 hours at 20°C, and produces substantial amounts of the diastereomeric 4-ethoxy-2-methylcyclopentanones, even in the presence of a 10-fold excess of benzoquinone. A potential reason is that this substrate provides an oxygen chelate which displaces benzonitrile. Opening of the chelate and subsequent rearrangement produces palladium(II) with tetrahydrofuran or benzoquinone²⁰ as potential ligands.

Table	Entry	Starting Material	Reference	Product ^a	Reference	% Yield ^b
	1		23		19	67
	2		23		21	67
	3		23		21	53
	4		23		22	58
	5		23		23	16
	6		23		23	20
	7 ^c		8		23	21
					23	42

^aA mixture of 1-vinyl-1-cyclobutanol (0.63 mmol), p-benzoquinone (1.26 mmol), and bis(benzonitrile)palladium dichloride (0.033 mmol) was refluxed in THF (16 mL) under a drying tube until the starting material was gone as judged by TLC (48-245 h). Extractive isolation included an aqueous dithionite wash to reduce the excess benzoquinone.

^bYield of chromatographically purified product.

^cStirred at room temperature.

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