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Pd^{II}-Catalyzed Cyclization of 1-Cyclopropyl-2-propynyl Acetates

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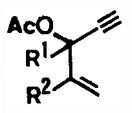
Dedicated to Professor Albert Eschenmoser on the occasion of his 60th birthday

Abstract: $PdCl_2(MeCN)_2$ catalyzes the cyclization of 1-cyclopropyl-2-propynyl acetates to 3-methyl-1,4-cyclopentadienyl acetates, which are cleaved in situ to 2-cyclopentenones.

$PdCl_2(MeCN)_2$ catalyzes the cyclization of 1-ethynyl-2-propenyl acetates **1** to 1,4-cyclopentadienyl acetates **2** which are cleaved in situ to 2-cyclopentenones **3**[1].



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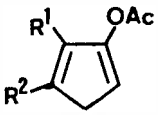

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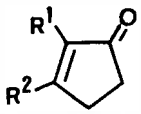

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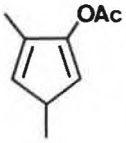

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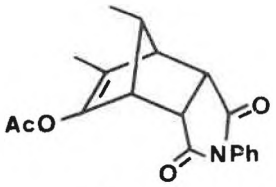
This paper reports that the double bond in **1** can be replaced by a cyclopropane ring. The cyclization then leads to 3-methyl-1,4-cyclopentadienyl acetates.

Thus treatment of **4**, 0.5 M in toluene, with 0.1 equiv. of $PdCl_2(MeCN)_2$ and 3 equiv. of *N*-phenylmaleimide at 60 °C for 8 h gave the adducts **6** and **7** in a ca. 4:1 ratio and near-quantitative yield.

The adducts were isolated by column chromatography and separated by fractional crystallization. The orientations of the methyl groups on the bridges were assigned on the basis of the expected reactivity of the trapped cyclopentadiene **5**.

Treatment of **4**, 0.8 M in acetonitrile, with 0.21 equiv. of $PdCl_2(MeCN)_2$ at 60 °C for 7 h followed by distillation afforded the cyclopentenones **8** and **9** in a 1.6:1 ratio and 89% combined yield (GC analysis of the distilled material).



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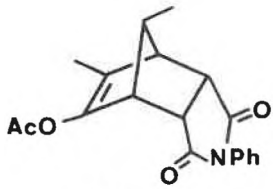

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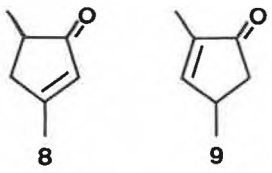
In the same fashion, **10** was converted into **11** and **12** (ratio 1:4, combined yield 55%). An extension of the type of mechanism proposed for **1**→**2** can be formulated, and there is ample precedent for the ring contraction **13**→**14**[2].



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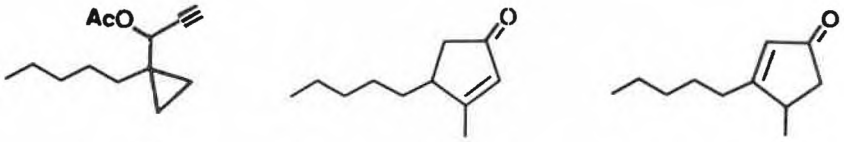

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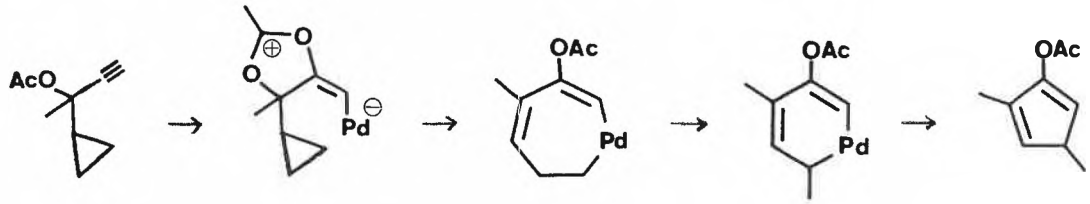

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[1] V. Rautenstrauch, *J. Org. Chem. 49*, (1984) 950; see also *Chimia* 39 (1985) 225, and references therein.
[2] R.C. Larock, S. Varaprath, *J. Org. Chem. 49* (1984) 3432, and references therein.