2. Palladium(0)-Catalyzed Cyclizations of Simple 1-Aryl-1,7-octadien-3-yl Acetates

Preliminary Communication[1])

by **Wolfgang Oppolzer***, **Rolf E. Swenson**, and **Werner Pachinger**

Département de Chimie Organique, Université de Genève, CH-1211 Genève 4

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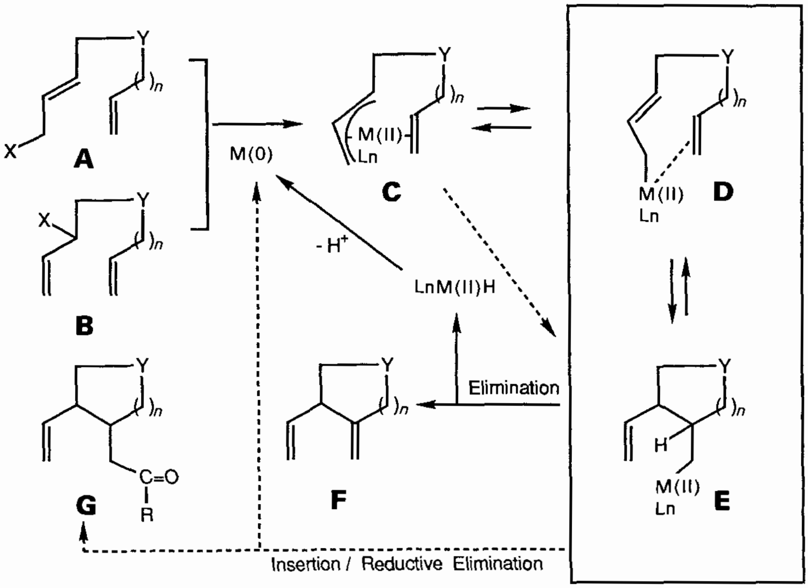
Dienyl acetates **2** lacking a geminal disulfone or a malonate group cyclize selectively to (*E*)-1-methylidene-2-styrylcyclopentanes **4** in the presence of 7 mol-% of [Pd(PPh$_3$)$_4$].

Pd(0)- [1], Pt(0)-, and Ni(0)-catalyzed [2] cyclizations of 1-acetoxy-, 1-tetrahydropyranyloxy-, 1-bromo-, and 1-iodo-2,7-octadienes (or -2,8-nonadienes) **A** exemplify part of a new stereospecific methodology leading to an array of carbo- and heterocycles **F** *(Scheme 1)*. Precursors **A** containing the allyl or the enophile unit as part of a ring gave

Scheme 1



X = AcO, OH, THPO, Br, I
Y = $(SO_2Ar)_2C$, $(CO_2Me)_2C$, RN, O
n = 1, 2
M = metal

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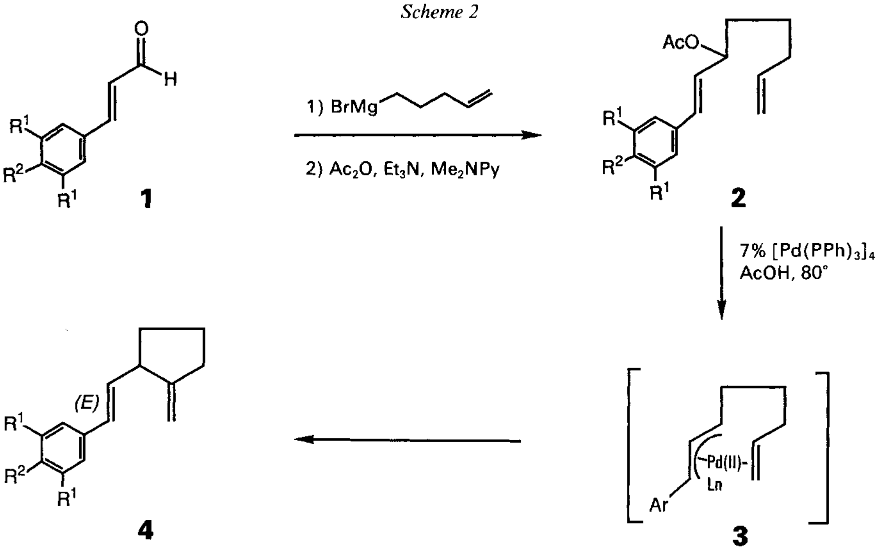
[1]) Presented *(W. O.)* at the '3e Congrès national de la Société Française de Chimie', Nice, September 5, 1988.

annulated ring systems. The experimental results are consistent with a *cis*-allylation of the alkene bond by a σ-allylmetal (**D**→**E**) or π-allylmetal unit[2]) (**C**→**E**) and a β-elimination with subsequent regeneration of the metal(0) catalyst. CO insertion reactions into **E** afforded monocyclic esters **G** (R = MeO) and in some cases (*via* **G**, R = NiLn) bicyclic annulated cyclopentanones with 'concomitant' stereocontrolled formation of four C–C bonds [2]. However, all educts **A** described so far contained either a $(SO_2Ar)_2C$, malonate, N, or O functionality Y which (for entropic reasons) may assist the cyclization process. These functional groups also facilitate the preparation of the precursors **A** and can be readily removed [4] or modified; nevertheless, it remained to be clarified, whether they are essential for the cyclization **D** (**C**)→**E** or not.

We report here that 1,7-octadien-3-yl acetates **B** containing a simple C-bridge Y are very easily accessible and undergo smooth Pd(0)-catalyzed ring closures. Our results are summarized in *Scheme 2* and the *Table*.

Scheme 2



a $R^1 = R^2 = H$; **b** $R^1 = H$, $R^2 = CF_3$; **c** $R^1 = CH_3O$, $R^2 = H$

Table. *1,7-Octadien-3-yl Acetates* **2** *and their* $[Pd(PPh_3)_4]$*-Catalyzed* (7 mol-%, AcOH, 80°) *Cyclization to* **4**

Entry	R^1	R^2	Yield [%] of **2** from **1**	Cyclization time [h]	Yield [%] of **4** from **2**
a	H	H	68	8	49
b	H	CF_3	70	2	67
c	MeO	H	64	3	94

Addition of (*E*)-cinnamaldehydes **1** to pent-4-enylmagnesium bromide (1.1 mol-equiv., THF, 0°→r.t., 4 h; aq. workup) followed by 4-(dimethylamino)pyridine-catalyzed acetylation (1.5 mol-equiv. Ac_2O/Et_3N, 0.02 mol-equiv. Me_2NPy, THF, r.t., 4–18 h)

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[2]) For the formation and other reactions of allylpalladium intermediates, see [3].

furnished dienyl acetates **2** in good yields. Heating the phenyl-substituted acetate **2a**[3]) in AcOH in the presence of 7 mol-% of $[Pd(PPh_3)_4]$ at 80° for 8 h followed by aq. workup and flash chromatography (SiO_2, pentane) gave **4a**[3]) in 49% yield. No other product could be found in the reaction mixture. We then subjected the less volatile dienyl acetates **2b**[3]) and **2c**[3]) which carry electron-withdrawing or electron-donating aryl substituents, respectively, to similar cyclization conditions. Indeed, the expected 1-methylidene-2-styrylcyclopentanes **4b**[3]) and **4c**[3]) were isolated in 67 and 94% yield, respectively. In all three cases, *only* the (*E*)-product **4** (assigned *via* the ^{1}H-NMR coupling constant $J_{AB} = 16$ Hz) was observed. This indicates that among the rapidly equilibrating *anti*- and *syn*-allylpalladium intermediates[2]), it was the latter (*i.e.* **3** or the corresponding σ-allyl complex) which cyclized and determined kinetically the (*E*)-configuration of **4**. In support of this argument it was found that methyl oleate and (*Z*)-1-phenylhept-1-ene did not isomerize to their (*E*)-isomers on heating with $[Pd(PPh_3)_4]$ (7 mol-%) at 80° in AcOH for 16 h.

The scope and implications of these results are being further explored in our laboratories.

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[3]) Characterized by IR, ^{1}H-NMR (360 MHz), ^{13}C-NMR, and MS. The 4-(trifluoromethyl)benzaldehyde obtained from 4-(trifluoromethyl)benzyl alcohol (pyridinium chlorochromate, CH_2Cl_2, r.t., 2.5 h) was treated with (formylmethylidene)triphenylphosphorane (1.1 mol-equiv., toluene, 80°, 22 h) to give **1b**. Using identical conditions, **1c** was prepared from 3,5-dimethoxybenzaldehyde.