

Abnormal Pd^{II}-Catalyzed Cyclization of 1-Methyl-1-(2-trimethylsilylethynyl)-2-propenyl Acetate

Valentin Rautenstrauch*, Ulrich Burger, and Philippe Wirthner**

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

Abstract: PdCl₂(MeCN)₂-catalyzed cyclization of 1-methyl-1-(2-trimethylsilylethynyl)-2-propenyl acetate (**4**) afforded 5-methyl-2-trimethylsilyl-1,4-cyclopentadienyl acetate (**5**) and 3-methyl-2-trimethylsilyl-1,3-cyclopentadienyl acetate (**6**) in a 1.2:1 ratio and ≥ 80% combined yield. The formation of **5** was anticipated by analogy with previous work but that of **6** is unprecedented. Compounds **5** and **6** were trapped with *N*-phenylmaleimide and their fate in the absence of the trapping agent elucidated.

PdCl₂(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**; alkyl substituents on the ethynyl group are not compatible with the reaction^[1a].

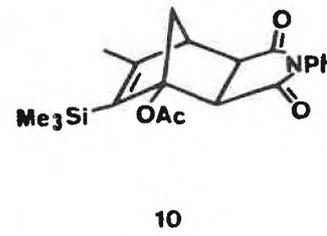
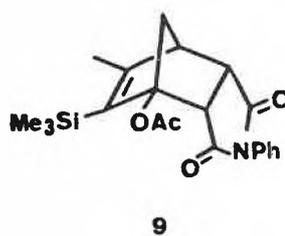
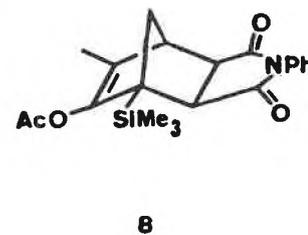
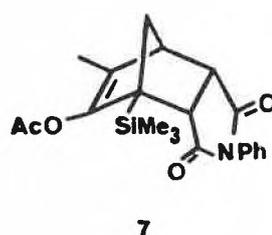
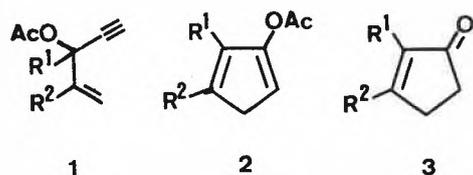
Thus treatment of **4**, 1.4 M in toluene, with 0.1 equiv. of PdCl₂(MeCN)₂ and 1 equiv. of *N*-phenylmaleimide at 80 °C for 90 min gave four adducts **7–10** which were isolated by column chromatography. The isolated yields of the *endo*-adducts **7** and **9**

temperature-dependent. This is due to hindered rotation about the acetate C–O bond.

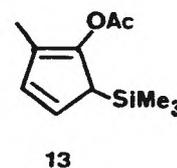
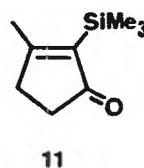
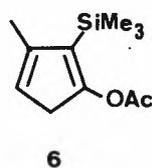
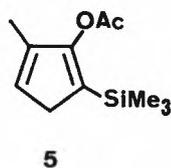
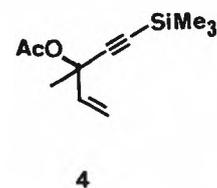
In the absence of the dienophile, **6** was cleaved as usual^[1a] to afford the cyclopentenone **11**, but **5** instead rearranged to give a mixture of isomers by [1,5] hydrogen and trimethylsilyl shifts, which could be isolated. In the presence of acetic acid, **6** was again deacylated and the cyclopentadienes derived from **5** both deacylated and desilylated.

Thus treatment of **4**, 0.9 M in acetonitrile, with 0.05 equiv. of PdCl₂(MeCN)₂ at 60 °C for 75 min followed by distillation gave **11** and a mixture of cyclopentadienes. The latter gave one broad peak on gas chromatography and exhibited a ¹H-NMR spectrum (ca. 15 °C) with partially broadened signals. Treatment of the cyclopentadiene mixture with PdCl₂(MeCN)₂ and acetic acid in acetonitrile (see below) gave **12**. Combination of these results with that of the trapping experiment indicates that the cyclopentadienes are isomers of **5** formed by [1,5] hydrogen^[2] and trimethylsilyl shifts^[2]. In principle, [1,5] hydrogen shifts can lead to four isomers, one of which (**13**) can in turn rearrange to give four further isomers by [1,5] trimethylsilyl shifts. Which isomers dominate was not investigated. The yields of **11** and the cyclopentadienes were 37% and 46%, respectively (GC analysis of the distilled material).

Treatment^[1a] of **4**, 0.8 M in acetonitrile, with 0.1 equiv. of PdCl₂(MeCN)₂ and 1 equiv. of acetic acid at 60 °C for 50 min –



We have now found that a trimethylsilyl substituent on the ethynyl group changes the course of the cyclization, acetate **4** giving two cyclopentadienes **5** and **6** in a 1.2:1 ratio and ≥ 80% combined yield. Cyclopentadiene **5** was expected by analogy with **1**→**2**. The formation of the 1,3-cyclopentadienyl acetate **6**, in which the acetoxy and trimethylsilyl groups are interchanged with respect to **5**, is without precedent and difficult to explain.



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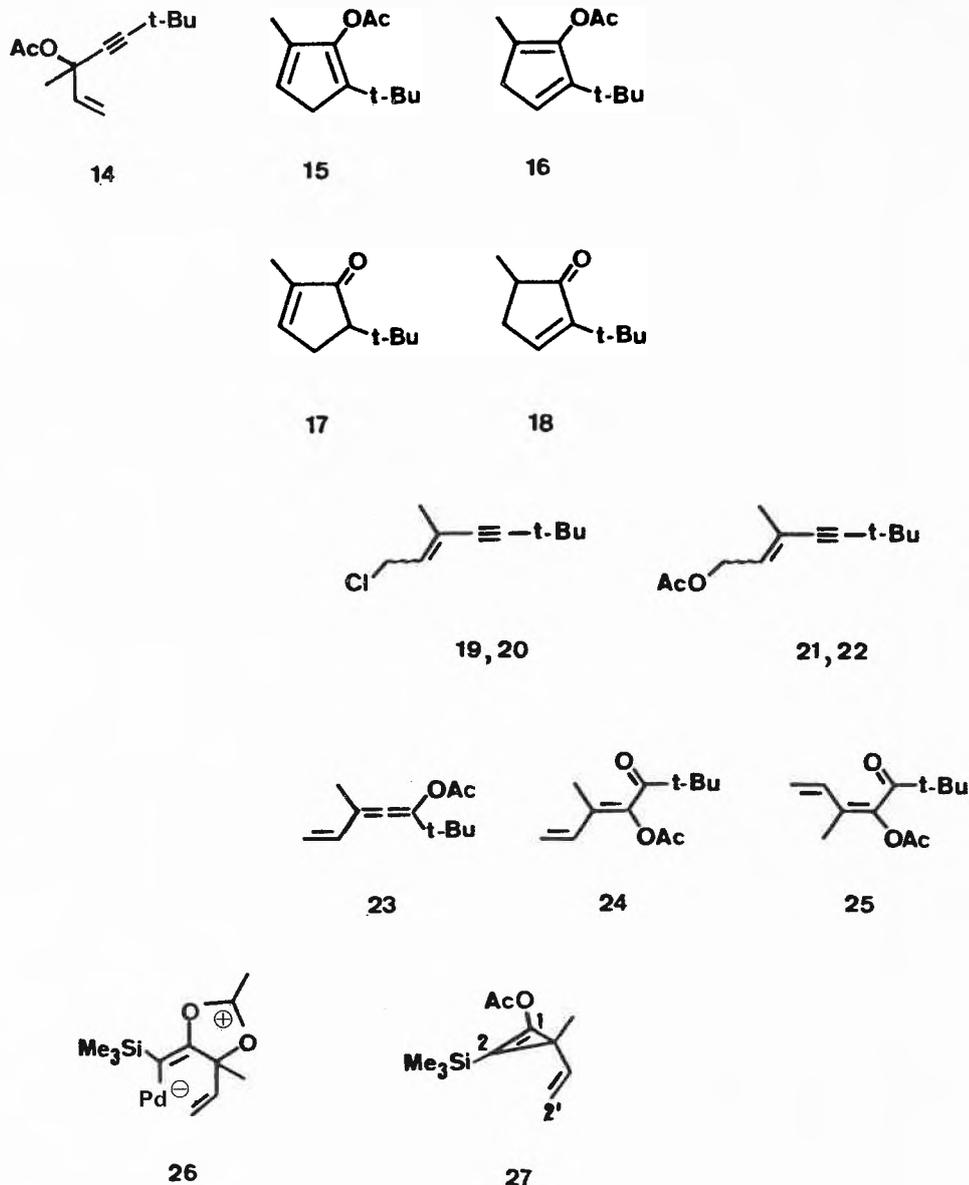
** Prof. Dr. U. Burger, P. Wirthner, Département de
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were 44% and 36%, respectively. The *exo*-adducts **8** and **10** were minor products and their exact yields were not determined. The structure of **10** was difficult to establish because its ¹H-NMR spectrum is strongly

the conditions also used for the deacylation and desilylation of the cyclopentadienes derives from **5** – and work up^[1a] directly afforded **11** and **12** in 18% and 44% yields, respectively (GC).

In contrast, even the *tert*-butyl analogue **14** only gave the normal set of cyclopentadienes in low yield, plus side-products. Thus treatment of **14**, 1.0 M in acetonitrile, with 0.1 equiv. of $\text{PdCl}_2(\text{MeCN})_2$ at 80°C for 2 h furnished a mixture of cyclopentadienes giving a sharp peak on gas chromatography. The $^1\text{H-NMR}$ spectrum (ca. 15°C) of the mixture suggests that the main components are **15** and **16**. This was confirmed by lithium aluminum hydride reduction and hydrolysis which afforded **17** and **18**. There was no deacylation under the conditions of the cyclization (even with acetic acid present) and also no discernible reaction with *N*-phenylmaleimide. The yield of the cyclopentadienes was only about 4% (GC). They were isolated by distillation and column and gas chromatography. In the same way were isolated a number of other products, namely, the primary chlorides **19**, **20** and acetates **21**, **22**, the allene **23**, and the acetoxyketones **24**, **25**^[1]. The yields of these products were also low (0.05–4%, GC).

The transformation of **4** into **6** is difficult to reconcile with the earlier mechanistic hypotheses^[1]. The only reasonable explanation we have is that a vinylcyclopropene **27**, or an organometallic equivalent^[3,4], is an intermediate, thus $4 \rightarrow 26 \rightarrow 27 \rightarrow 5 + 6$. Vinylcyclopropene-cy-



clopentiadiene rearrangements^[4] could proceed by formation of bonds between C-2' and C-1 ($\rightarrow 6$), and C-2' and C-2 ($\rightarrow 5$) here and only between C-2' and the unsubstituted C-2 in the case of $1 \rightarrow 2$. This hypothesis requires that the trimethylsilyl and acetoxy groups remain bound to the same carbon atoms as in **4**^[5], and this could be checked by a labeling experiment.

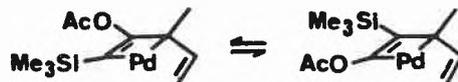
Our hope to find the same anomaly in the case of **14** was not realized but this negative result is inconclusive.

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[1] a) V. Rautenstrauch, *J. Org. Chem.* 49 (1984) 950; Note 7 in this paper should have included: M. Rosenblum, *J. Am. Chem. Soc.* 79 (1957), 3179; b) V. Rautenstrauch, *Tetrahedron Lett.* 25 (1984) 3845.

[2] Review: J.H. Gajewski: *Hydrocarbon Thermal Isomerizations*, Academic Press, New York 1981, p. 71–74.

[3] That two interconverting palladiacyclobutenes are intermediates:



[4] To our knowledge, there is only one report of a thermal vinylcyclopropene-cyclopentadiene rearrangement: R. Breslow, in P. de Mayo: *Molecular Rearrangements*, Wiley-Interscience, New York 1963, part I, p. 236. The related thermal 3-phenylcyclopropene-indene rearrangement is better known: M.A. Battiste, B. Halton, R.H. Grubbs, *J. Chem. Soc. Chem. Commun.* (1967) 907; I.N. Domnin, R.R. Kostikov, A. de Meijere, *Zh. Org. Khim.* 19 (1983) 2206. This rearrangement is catalyzed by Pt^{II} , Cu^{I} , and Pd^{II} salts: J.A. Walker, M. Orchin, *J. Chem. Soc. Chem. Commun.* (1968) 1239; A.S. Monahan, J.D. Freilich, J.-J. Fong, *Tetrahedron Lett.* (1970) 1865; R.A. Fiato, P. Mushak, M.A. Battiste, *J. Chem. Soc. Chem. Commun.* (1975) 869.

[5] As opposed to a mechanism in which the substituents change places.