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PALLADIUM (II) - CATALYZED REARRANGEMENT OF ALLYLIC ACETATES [1]

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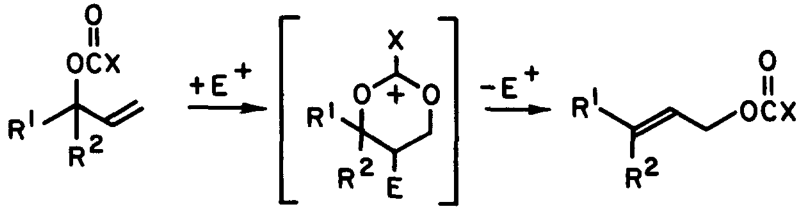
We recently reported that mercuric trifluoroacetate was an effective catalyst for equilibrating carbamic esters of allylic alcohols at room temperature ($1 \rightleftarrows 3$, X=NMe$_2$).[3,4] Yields were uniformly high, and side-reactions (elimination, cyclization, and skeletal rearrangement) occasionally encountered in "classical" acid-catalyzed methods[5] of transposing allylic oxygen functionality were not observed. The mercuric trifluoroacetate catalyzed reaction was demonstrated to be intramolecular, and was suggested to proceed *via a cyclization-induced rearrangement* pathway ($1 \rightarrow 2 \rightarrow 3$, $E^+ = {}^+HgOCOCF_3$).[3,4,6] We also noted that other "soft" electrophiles might behave similarly. A palladium (II) catalyzed allylic ester rearrangement has been reported by Henry[7], although synthetic exploitations of this observation have not to our knowledge been recorded. In this letter we report that soluble palladium (II) salts are more effective than mercuric trifluoroacetate in promoting the rearrangement of allylic esters. In particular, we report that catalytic amounts of bis(acetonitrile)palladium(II) chloride equilibrates allylic acetates ($1 \rightleftarrows 3$, X=CH$_3$) at room temperature and in high yield.



1 2 3

Although the N,N-dimethylcarbamic ester of 3,7-dimethyl-1-octen-3-ol was completely rearranged within four hours when treated in tetrahydrofuran (THF) with 0.3 equiv of mercuric trifluoroacetate,[3] the corresponding acetate 4 was recovered unchanged after 24 hr under identical conditions.[8] In contrast, treatment of a THF solution of acetate 4 with *0.04 equiv* of bis(acetonitrile)palladium (II) chloride gave within 2 hrs the allylically rearranged acetate 5 (99% yield, a 78:22 **E**:Z mixture, by GLC analysis). Concentration, and bulb-to-bulb distillation afforded 5 in 88% isolated yield. The results obtained when a representative group of allylic acetates were treated similarly are summarized in Table 1.[9] The palladium(II) catalyzed rearrangement is highly **E**-stereoselective. *Trans*-cinnamyl acetate (8) was produced with an isomeric purity of 98%, and the 78:22 **E**:Z ratio observed for 5 is unusually high for the formation of allylic esters of this type.[3,5] Advantages of the mild palladium (II) catalyzed rearrangement are well illustrated in the high yield conversion of 6 → 7, since the alcohol corresponding to 6 was reported[10] to yield dienes as major products when allylic rearrangement was attempted under acid-catalyzed solvolytic conditions. The only limitation we have encountered to date are low conversions with linalyl acetate, which we tentatively attribute to the formation of diene palladium(II) complexes.

As a result of the mildness of the reaction conditions, ease of product isolation, and high yields, the palladium (II) catalyzed allylic acetate rearrangement will likely be the method of choice for many allylic oxygen interconversions. Details of the mechanism of this catalyzed rearrangement, and other examples of palladium(II)-catalyzed allylic rearrangements, will be reported in due course.

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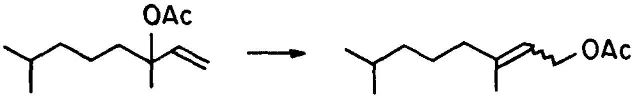
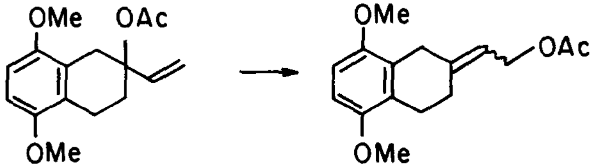
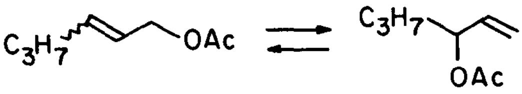
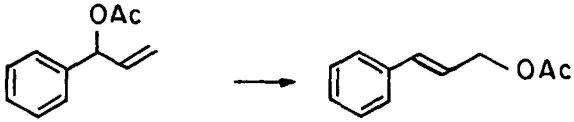
TABLE I. Palladium (II) Catalyzed Allylic Acetate Rearrangements.[9]

CONVERSION	CONDITIONS	YIELD(%)
 4 5	0.04eq, 2hr	88
	0.04eq, 2hr	93
 6 7	0.04eq, 1hr	87
 59% 41%	0.04eq, 2hr	95
 8	0.01 eq, 8hr	96

References and Notes

1. Catalyzed Sigmatropic Rearrangements. 4. For part 3 see reference 3.

2. A.P. Sloan Foundation Fellow, 1975-77; Camille and Henry Dreyfus Teacher-Scholar Award Recipient, 1976-81.

3. L.E. Overman, C.B. Campbell, and F.M. Knoll, *J. Am. Chem. Soc.*, **100**, 4822 (1978).

4. L.E. Overman and C.B. Campbell, *J. Org. Chem.*, **41**, 3338 (1976).

5. Cf. R.H. DeWolfe and W.G. Young in "The Chemistry of the Alkenes," E.S. Patai, Ed., Interscience, New York, N.Y., 1964, Chapter 10; see also references cited in reference 3.

6. The intramolecularity of the mercury (II)-catalyzed reaction has been exploited: (a) A. Eschenmoser, Peter A. Leermakers Symposium Lecture, Wesleyan, Conn., May, 1977; (b) B.M. Trost, J.M. Timko, and J.L. Stanton, *J. Chem. Soc. Chem. Commun.*, 436 (1978).

7. P.M. Henry, *J. Am. Chem. Soc.*, **94**, 5200 (1972).

8. Mercuric trifluoroacetate catalyzed allylic acetate rearrangements do occur at a reasonable rate in refluxing THF: R. Knoll, unpublished observations; and reference 6a.

9. Reactions were conducted under a nitrogen atmosphere with an ester concentration of 0.1 *M*. Yields refer to isolated material of purity greater than 97% as determined by GLC analysis. Reaction conditions were optimized for the formation of **8** only. Bis (benzonitrile) palladium(II) chloride is equally effective, but less convenient, since some contamination of the product by benzonitrile results.

10. T.H. Smith, A.N. Fujiwara, W.W. Lee, H.Y. Wu, and D.W. Henry, J. Org. Chem., **42**, 3653 (1977).

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