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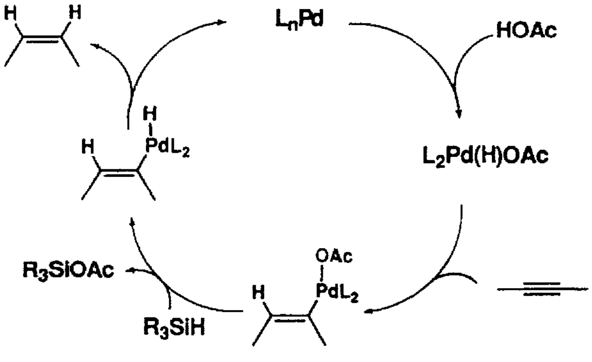
# A Convenient Chemoselective Semihydrogenation of Acetylenes Using Homogeneous Catalysis

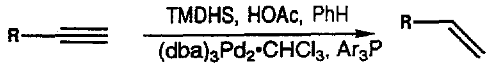
Barry M. Trost* and Rebecca Braslau
Department of Chemistry
Stanford University
Stanford CA 94305

**Summary.** Acetylenes and some dienes are rapidly reduced to olefins by a combination of acetic acid and a silicon hydride in the presence of a Pd(0) catalyst.

Whereas heterogeneous palladium catalyzed hydrogenation constitutes an immense field of endeavor,[1,2] homogeneous palladium catalyzed reductions are now only emerging as useful synthetic processes.[3-8] Hydrogenolyses of halides[3] and allyl or propargyl carboxylates[4] exemplify very useful transformations of this type. Palladium(0) catalyzed reductions of conjugated double bonds which employ tin hydrides[7] and, occasionally, silicon hydrides[8] presumably initiate via a hydrostannation or hydrosilylation followed by a protonolysis with water. Our discovery of a reductive cyclization of 1,6-enynes using acetic acid and a silane catalyzed by a Pd(0) complex[9] suggested a mild method to effect acetylene reductions according to the following catalytic cycle. The lack of reactivity of olefins to the Pd(0) - acetic acid catalyst system suggested such a process might be intrinsically more chemoselective compared to heterogeneous catalysts.



Monosubstituted acetylenes 1-3 were initially examined (eq 1). As a standard set of reaction conditions, the alkyne was added to a benzene solution containing 2.5 mol% $(dba)_3Pd_2\ CHCl_3$,[10] 10 mol% tri-o-tolylphosphine, 1 mol of TMDHS,[10] and 1 mol of HOAc. The reaction was terminated when analysis revealed consumption of starting material. Normally, the reaction was complete within 30 min. at ambient temperature. The malonate substrate required the addition of silica gel to the reaction mixture to promote reduction. In the

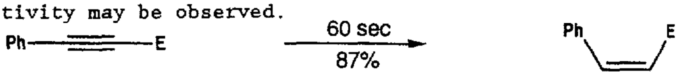


(1)

| | | | | |
|---|---|---|---|---|
| 1 | R = | $PhOCH_2$ | 6 min | 95% |
| 2 | R = | $DMPSO(CH_2)_4$ | 22 min | 72% |
| 3 | R = | $(CH_3O_2C)_2CHCH_2$ | 1 min | 65% |

absence of the silica gel in this unique case, a product forms that slows reduction. Addition of silica gel reverses the formation of this, as-yet, unidentified product.

The stereochemistry was explored with disubstituted acetylenes. As shown in eq. 2-4, good *cis* selectivity may be observed.



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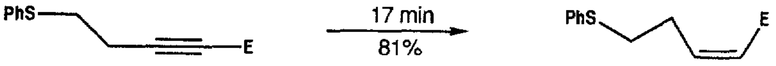
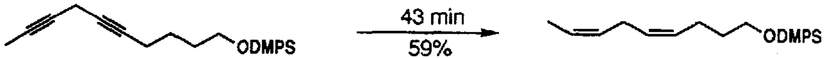


(3)

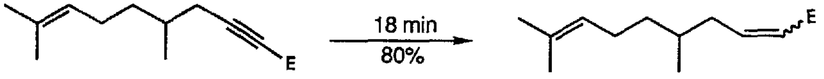
(4)



4

The product of the last example, a model for the skipped dienes of the arachadonic acid cascade, is a 13.4:1 ratio of the Z,Z-diene 4[11] compared to another product. The Z sterochemistry of the 8,9-double bond of 4 is assigned from the 10.7 Hz observable vinyl coupling. The assignment of the sterochemistry of the 5,6-double bond stems from the upfield position of the $^{13}C$ signal for the allylic carbons [i.e. C(4) at $\delta$ 26.9 and C(7) at 25.8] due to steric compression compared to the *trans* olefins which show signals for such carbons at $\delta$ 32-34.[12]

Unfortunately, such *cis* selectivity is not universal. Reduction of ynoate 5 produces a final mixture of 2.6:1 of the Z and E enoates[11] (eq 5).



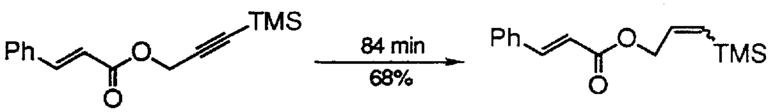
(5)

5

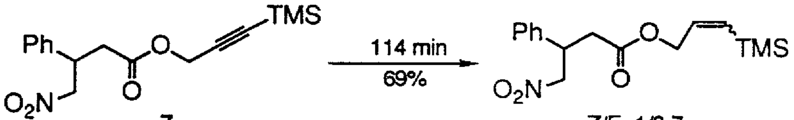
Z/E 2.6/1

Following the reaction by gas chromatography indicates that during reaction, the Z-isomer is initially generated cleanly. Isomerization of the kinetic product occurs during extended reaction times, quenching, work-up, and/or purification. Z:E ratios as high as 6.8:1 have been observed prior to final purification. The source of the equilibration has not been determined, as yet. All attempts to suppress it have not been completely successful.

This isomerization is not limited to ynoate substrates. 5-Decyne also produces Z,E mixtures, as did the silyl acetylenes 6[11] and 7[11] (eq 6 and 7). The latter two examples, however, dramatically illustrate the chemoselectivity. Nitro groups and conjugated double bonds are among the groups most easily reduced under conditions of heterogeneous catalysis. Neither interferes with this reduction.

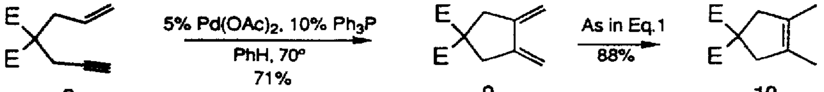


**6** Z/E 1/2 (6)

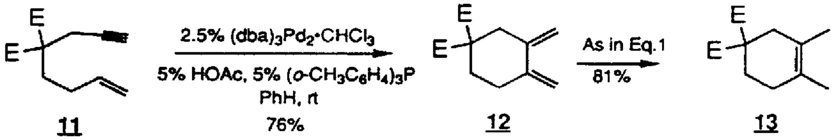


**7** Z/E 1/3.7 (7)

In an ancillary study, we also briefly examined the reduction of cisoid 1,3-dienes that are easily prepared by our metal catalyzed cycloisomerization reactions as shown in eq 8[13] and 9.[14,15]



**8** **9** **10** (8)



**11** **12** **13** (9)

Thus, using either our Pd(+2) conditions for the 1,6-enyne **8** or our Pd(0)-acetic acid conditions for the 1,7-enyne **11** provides the five and six membered ring cisoid dienes 9[11] and 12.[14] Because of the extraordinary sensitivity of the cyclopentane **9**, addition of 5 mol % of BHT to the usual conditions led to a substantial improvement in yield. In both cases, only the 1,4-reduction products 10[11] and 13[11] were obtained - presumably a reflection of thermodynamic factors. This sequence constitutes a useful strategy to such cycloalkenes from acyclic precursors. The sequence of eq 9 is particularly intriguing since the cycloisomerization and reduction catalysts are identical. Thus, a one-pot procedure may be envisioned in which, upon completion of the cycloisomerization, addition of stoichiometric amounts of acetic acid and the silicon hydride would effect direct formation of the cycloalkene 13 from enyne 11.

This method for reduction appears to be highly chemoselective and, in many instances, proceeds with good *cis* selectivity. Overreduction or reduction of other double bonds is normally not a problem nor is reduction of nitro groups. Only in the case of phenyltrimethylsilylacetylene was overreduction a problem and, in fact, complete saturation could be achieved in 70% yield by using 3 eq of acetic acid and 5 eq of TMDHS. The rapidity of the reduction and ease of operation combine with the excellent selectivity to make this method a useful one. It does also provide further chemical characterization for the Pd(0)-acetic acid catalyst systems. Mechanistic studies will be published in due course.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs.

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10. dba = dibenzylideneacetone, TMDHS = tetramethyldihdrodisiloxane

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