

Palladium(0)-catalysed Transfer Hydrogenation of Alkynes to *cis*-Alkenes with HCO₂H–NEt₃

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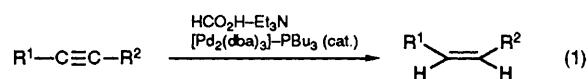
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Transfer hydrogenation of alkynes using HCO₂H–NEt₃ as a hydrogen donor in the presence of Pd⁰-catalyst proceeds highly stereoselectively to afford *cis*-alkenes in excellent yields, thus providing a practical method for conversion of alkynes to *cis*-alkenes.

Partial reduction of alkynes to *cis*-alkenes is important synthetically both in the laboratory and in industry.¹ Diimide reduction, catalytic reduction using molecular hydrogen, catalytic transfer hydrogenation using hydrogen donors other than molecular hydrogen, hydrometallation followed by hydrolysis and reduction with metal-proton donor reagents have been used for this purpose. In comparison with other methods, the catalytic transfer hydrogenation method has real and potential advantages.² It is convenient to carry out; no pressure vessels are needed, and simple stirring of the solution is all that is required. It has fewer safety problems and it is potentially very economic. This method, however, as a rule is inferior to other methods in selectivity and in yield. Catalytic transfer hydrogenation of alkynes using heterogeneous³ or homogeneous palladium catalysts⁴ constitutes a most successful endeavor; the reaction, however, affords in many cases a notable amount of *trans*-alkenes and alkanes (over reduced products). Since *cis*- and *trans*-alkenes and the corresponding alkanes are difficult to separate from each other, the development of more selective catalytic systems for hydrogen transfer reduction has been anticipated.

In contrast to the widely accepted belief that catalytic hydrogen transfer reduction of alkynes to alkenes lacks practicability and generality, we have now found that the reduction proceeds highly selectively affording *cis*-alkenes in excellent yields by using [Pd₂(dba)₃]-PBu₃ (dba = dibenzy-

lideneacetone) as a catalyst and HCO₂H–NEt₃ as a hydrogen donor,⁵ thus providing an operationally simple and general method for the reduction of alkynes to *cis*-alkenes [eqn. (1)]. The results are summarized in Table 1.†



Inspection of Table 1 reveals several features of the present hydrogen transfer reduction in terms of the scope and limitation and the stereoselectivity. (i) The reduction of internal alkynes proceeds with high intrinsic *cis* selectivity and in excellent yields. (ii) The reduction of terminal alkynes also stops at the stage of semi-hydrogenation, but the yield is moderate owing to the production of unidentified compounds(s). (iii) Under the reaction conditions, the *cis*-alkenes derived from conjugated alkynes such as α,β -unsaturated ester (run 3) or arylacetylene (run 4) have a tendency to suffer isomerization and reduction, and so, in these cases, the most

† The reaction was carried out under argon atmosphere as follows: to a solution of HCO₂H (88%, 6.0 mmol) and Et₃N (6.0 mmol) in tetrahydrofuran (THF; 2 ml) were added Pd₂(dba)₃·CHCl₃ (0.05 mmol) and Buⁿ₃P (0.20 mmol), and the mixture was stirred for 5 min. To this were added THF (6 ml) and an alkyne (2.0 mmol) and the mixture was stirred for the period indicated in Table 1 at 40 °C.

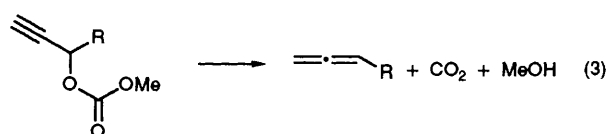
Table 1 The reaction of alkynes with HCO₂H-Et₃N in the presence of Pd⁰ catalyst

Entry	Substrate		Reaction time/h	Product			Total yield (%) ^b
	R ¹ -C≡C-R ²			Ratio (%) ^a			
	R ¹	R ²		<i>cis</i> -alkene	<i>trans</i> -alkene	alkane	
1	C ₈ H ₁₇	H	1	98		2	65 ^d
2	C ₈ H ₁₇	Me	2	97 (97)	3 3	<1 <1 ^c	~100 ^d
3	C ₅ H ₁₁	CO ₂ Me	2	98 (78)	2 19	<1 3 ^c	95 ^d
4	Ph	Et	3	89 (71)	5 11	6 18 ^c	~100 ^d
5	C ₅ H ₁₁	CH ₂ OH	2	97.5	2.5	<1	78
6	C ₅ H ₁₁	CH ₂ OHP ^e	1.5	97	3	<1	96
7	C ₅ H ₁₁	CH ₂ OTBS ^e	2	95.5	4.5	<1	92
8	C ₅ H ₁₁	CH(OH)Et	3	97.5	2.5	<1	90
9	Et	(CH ₂) ₃ OH	2.5	98	2	<1	77

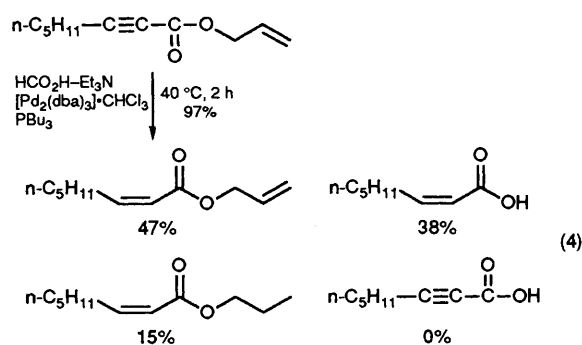
^a Determined by GC and/or ¹H NMR analysis. ^b Unless otherwise indicated, isolated yield. ^c Allowing the reaction to run for further several hours after the completion of the reaction (total 6 h for entry 2, 15 h for entry 3, 9 h for entry 4). ^d GC yield. ^e THP = tetrahydropyran-2-yl; TBS = *tert*-butyldimethylsilyl.

successful result can be obtained by cessation of the reaction at the time when all the alkynes are consumed.

The present reagent system, HCO₂H-NEt₃[Pd₂(dba)₃]-PBu₃, has been reported to be effective for hydrogenolysis of allyl esters to olefins and carboxylic acids,⁶ and of prop-2-ynyl methyl carbonates to allenes, CO₂ and MeOH⁷ as shown in eqns. (2) and (3), respectively. These results prompted us to

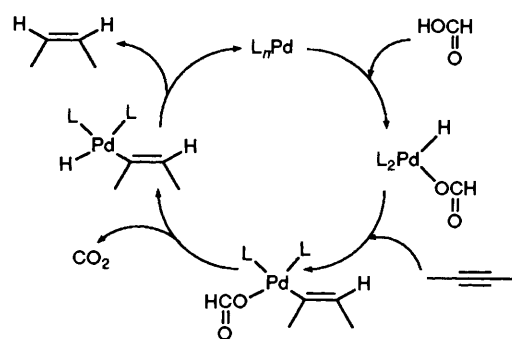
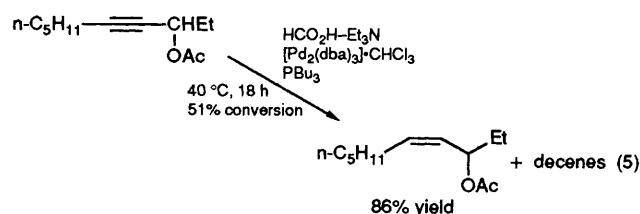


investigate the reaction of allyl alk-2-ynoates and prop-2-ynyl acetates, respectively. In both cases, the reduction of the triple bond was found to take preference over hydrogenolysis. Thus, as shown in eqn. (4) the reaction of allyl oct-2-ynoate afforded 47% yield of allyl (*Z*)-oct-2-enoate, 15% of *n*-propyl (*Z*)-oct-2-enoate and 38% of (*Z*)-oct-2-enoic acid. Although (*Z*)-oct-2-enoic acid can be produced *via* hydrogenolysis followed by reduction, the absence of oct-2-ynoic acid in the reaction products strongly indicates that it is formed *via* hydrogenolysis of allyloct-2-enoate.



Similarly 3-acetoxydec-4-yne was converted into (*Z*)-3-acetoxydec-4-ene and its hydrogenolysis product (decenes), but less than 5% of allene compounds were produced if any eqn. (5).[‡]

[‡] Alk-2-ynyl acetates were reported to afford a mixture of the corresponding 1,2-dienes (allene compounds) and alk-1-enes by using HCO₂NH₄[Pd₂(dba)₃]-PBu₃; see ref. 7.

**Scheme 1**

Although mechanistic details of the present catalytic transfer reduction must await active investigation, a reasonable mechanistic hypothesis is given in Scheme 1.

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