

Selective Synthesis of Alkynes by Catalytic Dehydrogenation of Alkenes over Polymer-supported Palladium Acetate in the Liquid Phase

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A heterogenized palladium acetate catalyst, in the presence of oxygen and perchloric acid in ethanol–water caused the direct conversion of terminal and internal monoalkenes into the corresponding alkynes, under mild conditions and in high yields; Wacker-type ketonization occurs with the same reagents in dioxane–water.

Supporting catalytic species on insoluble organic polymers combines the advantages of both homogeneous and heterogeneous catalysis,¹ and is known to induce changes in the reactivity and selectivity of a number of important reactions, including oxidations.²

Our interest in this field³ has led us to investigate the Wacker-type reaction, which is one of the most important homogeneous processes for catalytic oxidation of alkenes. The different palladium and co-metal derivatives used as soluble catalysts, as well as the reaction medium, all serve to determine the nature of the products obtained; for example, carbonyl compounds are produced with palladium chloride in water as the liquid phase, while similar experimental conditions but in alcohols give mainly acetals.⁴

We have tried a different approach by resorting to metal (*e.g.*: Pd, Pt, or Rh) acetates bound to an insoluble aromatic oligoamide,⁵ a type of catalytic system which could behave as if it were in solution although operating as a separate phase.³ We have found that these 'heterogenized' homogeneous transition metal derivatives show good catalytic activity and stability, and some of them are efficient in catalysing the conversion of alkenes to yield products with a distribution rather different from those so far reported;⁴ the appropriate conditions (*vide infra*) make it possible to obtain either alkynes or ketones as the main products. We now describe the first example of one such oxygen-based selective dehydrogen-

ation of alkenes to alkynes, in the presence of supported palladium acetate as the catalyst; experimental conditions are exceedingly mild and yields are high.[†]

In a typical procedure, air was bubbled (3.5 l h⁻¹) through a magnetically stirred suspension of the appropriate amount of the supported palladium acetate catalyst[‡] in a solution of the alkene (1) (3.0 mmol) and 70% aq. HClO₄ (2 ml) in 48 ml of solvent mixture (see Table 1 for details) at constant tempera-

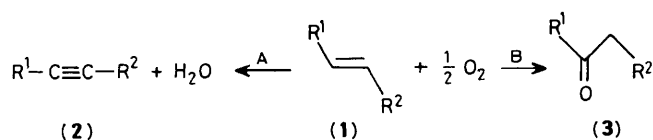
[†] Thermolytic elimination of hydrogen from alkenes is known to occur, but requires severe conditions and is confined to compounds with only a few carbon atoms.⁶

[‡] The catalyst was prepared by wet impregnation of an insoluble co-oligomeric species, oligo-*p*-phenyleneterephthalamide (OPTA),⁵ with a water–acetic acid solution (9 : 1) of palladium acetate, at room temperature. Thermogravimetric analyses⁷ established the metal loading: a microsample of the catalyst, *i.e.* a transition metal derivative supported on the organic matrix, was desiccated and weighed in a thermal analysis apparatus (Perkin Elmer Mod. TGS-2). The temperature was then raised up to 950 °C until all volatile components thermally decomposed and evaporated off in an air stream. After cooling, the metal residue was weighed and compared to the amount of active species originally present in the catalyst system. In all runs catalysts with 1% (w/w) Pd on OPTA were used. The catalyst can be recycled several times without any noticeable diminution of activity.

Table 1. Pd(OAc)₂-OPTA-catalysed synthesis of alkynes (2) and ketones (3) from alkenes (1).

Alkene (1)	Solvent system ^a	[Pd]:[(1)]	Temp./°C	Reaction time /min ^b	% Conversion of (1) ^c	% Selectivity ^c	
						Alkyne (2)	Ketone (3)
a; R ¹ = H; R ² = Pr ⁿ	A	1:25	25	210	100	89	11
	A	1:25 ^d	25	240	99	—	99
	B	1:200	25	160	98	8	89
b; R ¹ = H; R ² = Bu ⁿ	A	1:25	55	220	99	89	10
	B	1:200	55	270	98	3	95
c; R ¹ = H; R ² = n-C ₅ H ₁₁	A	1:25	55	300	98	89	9
	B	1:200	55	300	98	8	90
d; R ¹ = H; R ² = n-C ₆ H ₁₃	A	1:25	70	220	100	90	8
	A	1:200	70	50	99	49	50
	B	1:25	70	240	78	36	42
	B	1:200	70	360	100	10	90
e; R ¹ = H; R ² = n-C ₇ H ₁₅	A	1:25	70	300	99	91	8
	B	1:200	70	300	98	12	86
f; R ¹ = H; R ² = n-C ₈ H ₁₇	A	1:25	70	540	100	92	8
	B	1:200	70	360	98	5	93
g; R ¹ = Me; R ² = n-C ₅ H ₁₁	A	1:25	70	45	97	97	—
	B	1:200	70	150	89	—	89
h; R ¹ = Et; R ² = Bu ⁿ	A	1:25	70	180	98	98	—
	B	1:200	70	210	66	—	66
i; R ¹ = R ² = Pr ⁿ	A	1:25	25	280	93	91	—
	A	1:25	70	100	97	95	—
	B	1:200	70	110	32	—	32

^a A: ethanol (28 ml)–water (20 ml); B: dioxane (28 ml)–water (20 ml). ^b Corresponds to maximum conversion of (1). ^c Determined by g.l.c. analysis. ^d Catalyst: 1% w/w Pd, as Pd(OAc)₂–carbon.



ture; the reaction was monitored by quantitative g.l.c. analysis. At completion, the insoluble catalyst was filtered off, and the products were isolated by preparative chromatography and identified by i.r. and ¹H n.m.r. comparison with authentic samples. Results for a number of n-alkenes are given in Table 1.

One of the most interesting aspects of the reaction is the marked solvent effect. Thus, ethanol–water is the most effective medium among those examined for obtaining alkynes as the main products. Aqueous dioxane leads mainly to ketones, as expected from a palladium-catalysed oxidation. Addition of water and perchloric acid is essential to promote any catalytic activity in these reactions; control experiments showed that alkenes do not react as reported, either when the catalyst alone is suspended in anhydrous ethanol (or dioxane), or if one of these reagents is excluded.

Selectivity is another feature of these reactions, the nature and molar ratio of solvents as well as the catalyst being of importance. Accordingly, in ethanol–water (molar ratio 3:7), the terminal n-alkynes (2a–f) are obtained in very high yields from the corresponding alkenes, with limited formation of the methyl ketones (3a–f); isomerization of the alkene double

bond does not occur. Moreover, the *trans*-alkenes (1g–i) give nearly quantitative yields of the n-alkynes (2g–i), with full regioselectivity; again, neither isomerization nor ketonization occurs. These results differ from the reported behaviour of the palladium system, whereby regioselective control over the reactions of carbon–carbon double bond is difficult to achieve.⁸ Furthermore, in dioxane–water (molar ratio 2:8), the methyl ketones (3a–f) and dialkyl ketones (3g–i) are the main products, arising from highly regioselective oxidation of terminal and internal double bonds respectively, without formation of structurally isomeric carbonyl compounds; in this case, alkynes, when formed, are the by-products.

A likely reaction scheme for the alkenes investigated involves the early formation of solvated alkene–palladium(II) complexes,⁹ active in the conversion into alkynes and ketones, *via* two different paths, *i.e.*, an oxygen-based catalytic dehydrogenation and a Wacker-type oxidation cycle respectively. Formation of ketones might also result from acid-catalysed hydration of the alkynes, first obtained through the catalysed dehydrogenation step.[§]

In conclusion, our supported palladium catalyst shows promising synthetic potential, and its wide range of reactivity provides a valuable alternative approach to conventional

[§] Accordingly, n-alkynes (2d) and (2i) in dioxane–water are hydrated following Markownikov's rule to give only the ketones (3d) and (3i), under the conditions reported above (yields, *ca.* 85%); the latter products are detected in only minor amounts for reactions in ethanol–water.

routes for introducing a carbon-carbon triple bond into an organic structure.

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