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METAL-ASSISTED REACTIONS—PART 10[1]

RAPID, STEREOSELECTIVE AND SPECIFIC CATALYTIC TRANSFER REDUCTION OF ALKYNES TO *CIS*-ALKENES

ROBERT A. W. JOHNSTONE* and ANNA H. WILBY
The Robert Robinson Laboratories, The University, Liverpool L69 3BX, UK

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Abstract—The rapid, stereoselective, and specific transfer reduction of alkynes to alkenes using specially-modified, but easily prepared, palladium catalysts is described. Additional use of a phase transfer catalyst in these systems affords a simple method for phase transfer catalysed catalytic transfer reduction which can be carried out in the presence of other potentially reducible functional groups.

The reduction of alkynes to alkenes is an important reaction in synthetic organic chemistry because the alkyne grouping can be introduced readily into organic molecules[2] and its reduction to *cis*- or *trans*-alkene can be effected stereoselectively.[3] Many methods for this reduction have been described but probably only two are in widespread use. Hydrogenation of alkynes with molecular hydrogen and specially modified palladium catalysts can afford excellent yields of *cis*-alkenes[3] whilst dissolving metal reduction with an alkali metal in liquid ammonia yields *trans*-alkenes.[3] Following our earlier work on catalytic transfer reduction,[1] we describe here a simple alternative stereoselective and specific reduction of mono- and disubstituted alkynes to alkenes; with disubstituted alkynes, this reaction yields the *cis*-isomer almost exclusively.

Catalytic transfer reduction, the process whereby an organic or inorganic donor, through use of a catalyst, is used to provide hydrogen for reduction of an acceptor is a convenient, rapid, and frequently highly selective technique. The actual mechanism of transfer reduction is not clear[4] but it is not simply an alternative to reduction by molecular hydrogen.[4,5] Usually, if significant evolution of hydrogen is observed during transfer reduction, the yield of reduction product is low. Conversely, when evolution of hydrogen is not readily apparent, reduction may be rapid and high yielding. Further, transfer reduction shows different selectivity towards functional groups from that shown in catalytic reduction with molecular hydrogen. There follows further discussion of these points in relation to the catalysts and donors used in the work described here.

Donors

Of the donors that have been used most frequently in transfer reduction (cyclohexene, hydrazine, formic acid and formates, phosphinic acid and phosphinates, phosphorous acid and phosphites, alcohols and amines), we have found that sodium phosphinate is the most suitable for the rapid, clean reduction of alkynes to alkenes at room temperatures. The other donors listed above led either to no reduction or to poor yields of alkene over long intervals of time. Phosphinic acid proved not to be as good as sodium phosphinate as a donor in this system and this strongly suggests that the much higher redox potential of (naturally alkaline) aqueous sodium phosphinate (1.57V)[6] than that of the free acid (0.5V)[6] is necessary to effect reduction (the redox potential for the alkyne/alkene system is approximately 0.73V).[6] Reduction of alkenes to alkanes (redox potential, 0.52V)[6] is easier and, accordingly, any catalyst used to reduce alkynes to alkenes must be capable of bonding alkyne but not alkene to avoid complete reduction. The development of suitable catalysts for controlled reduction to alkene is described below.

Phase transfer catalysis

Because sodium phosphinate is readily soluble in water but not in organic solvents, a two-phase aqueous/organic solvent system was used in the experiments described here. The heterogeneous catalyst usually settles at the interface of the solvents and, to effect a better transfer of phosphinate anion to the catalyst, a phase transfer catalyst, benzyltriethylammonium chloride was added.

$$\mathrm{PhCH_2\overset{+}{N}Et_3\ Cl^- + H_2PO_2^- \rightleftharpoons PhCH_2\overset{+}{N}Et_3\ H_2PO_2^- + Cl^-} \qquad (1)$$

That the phase transfer catalyst afforded a smooth transfer of donor to the catalyst surface was evident in the greatly improved course of the reduction. This phase transfer catalysed catalytic transfer reduction technique was found to be useful in other situations. For example, octanoic acid is a suitable phase transfer catalyst for two-phase aqueous/organic solvent systems when the basic donor, hydrazine, is used with a heterogeneous catalyst.

Catalysts

The heterogeneous catalysts used for transfer reduction of alkynes in this work are based entirely on metallic palladium. Other transition metals commonly used as catalysts (e.g. Pt, Rh, Ru) were found to be inactive under these conditions. However, palladium alone was too active a catalyst so that specific reduction of alkyne to alkene was impossible and reduction of alkyne to alkene and then to alkane proceeded at such rates that isolation of alkene in good yield became impossible. Either the required alkene was accompanied by a lot of starting material if the reaction was stopped before much alkane had been formed or was accompanied by a lot of alkane if the reaction was allowed to proceed until all the alkyne had reacted. Typical catalyst poisons such as dimethyl sulphide or thiophen reduced the overall rates of reaction without enhancing the specificity of reduction. Commercial Lindlar-type palladium catalyst,[7] which is used for the specific reduction of alkynes to alkenes

Table 1. Reduction of 1,2-diphenylethyne to 1,2-diphenylethene and 1,2-diphenylethane using mercury-modified palladium catalyst

Molar ratio[1] of Pd to Hg	Reaction time	% Yield of Products			
		1,2-diphenylethyne	cis-1,2-diphenylethene	trans-1,2-diphenylethene	1,2-diphenylethane
1 : 0	15min	0	0	0	100
1 : 0.025	25min	0	35	0	63
1 : 0.1	55min	0	45	0	55
1 : 0.3	1hr	0	70	0	25
1 : 0.4	1hr17min.	0	57	0	10
1 : 0.5	3hr40min	5	87	3	5
1 : 0.6	4 days	0	52	31	12
1 : 0.7	5 days	0	83	10	6
1 : 0.8	2 weeks	100	0	0	0
1 : 0.9					
1 : 1.0					

[1] All catalysts were prepared from commercial 10% Pd/C (w/w) catalyst by addition of the requisite molar quantity of mercury (see experimental).

[2] All reactions were carried out at room temperature (≃ 20°).

with molecular hydrogen, was successful for some transfer reductions but not all. Eventually, modified catalysts were prepared from commercially available palladium-on-charcoal catalyst. These modified catalysts were very effective, leading to rapid, stereoselective, and specific reduction of alkynes to alkenes; no double-bond migration was observed and, with disubstituted alkynes, *cis*-alkenes were obtained as products.

Modified catalysts

It is well-known that electrolytic overvoltage correlates with catalyst activity.[8] As the overvoltage for liberation of hydrogen from an electrode increases, the catalytic activity of the metal composing the electrode decreases. From the metals that give high overvoltages with palladium, it was decided to investigate mixtures of these with palladium as modified catalysts. These catalysts were prepared easily by precipitation of the metal from an aqueous solution of its salt by sodium tetrahydroborate directly onto commercially obtainable palladium-on-charcoal catalyst. The metal-modified palladium catalysts were washed and dried and could be stored indefinitely. Of the metals examined as modifiers (Pb, Hg, Co, Ni, Pt), only lead or mercury proved of value for this work.

The molar ratio of lead or mercury to palladium affected the course of transfer reduction quite markedly. Thus, for reduction of 1,2-diphenylethyne, a ratio of Hg to Pd of 1:1 gave a completely inactive catalyst whereas at a ratio of 0.025:1, the catalyst was very active but exhibited little specificity. Table 1 shows the effect of changing the ratio on the reduction of 1,2-diphenylethyne. An optimum specificity and rapidity of reduction of 1,2-diphenylethyne to *cis*-stilbene was observed at molar ratios of 0.4:1 to 0.6:1 of lead or mercury to palladium. The ease of modification of the activity of a commercially available catalyst and repeatability of results is advantageous in that optimum yields of alkene can be obtained in most situations by variations of this ratio. It is not clear wheather the modifying metal affects the d-band energy levels of the palladium metal and therefore affects the binding of the organic substrates or whether the colligative distribution of palladium atoms on the surface of the charcoal support is disturbed, or both. Theories concerning such electronic or topological modification of catalyst activity have been advanced.[9]

Stereoselective reduction of alkynes

Using sodium phosphinate as hydrogen donor in an aqueous tetrahydrofuran solvent system with a lead- or mercury-modified Pd catalyst afforded the stereoselective and specific reduction of alkynes, for which some results are shown in Table 2 The comparative variation in ease and specificity of reduction with modified catalysts for just one alkyne, 1,2-diphenylethyne is given in Table 1. Using the optimum conditions, this alkyne could be reduced stereoselectively to *cis*-1,2-diphenylethene (*cis*-stilbene) with the formation of only small quantities of 1,2-diphenylethane.

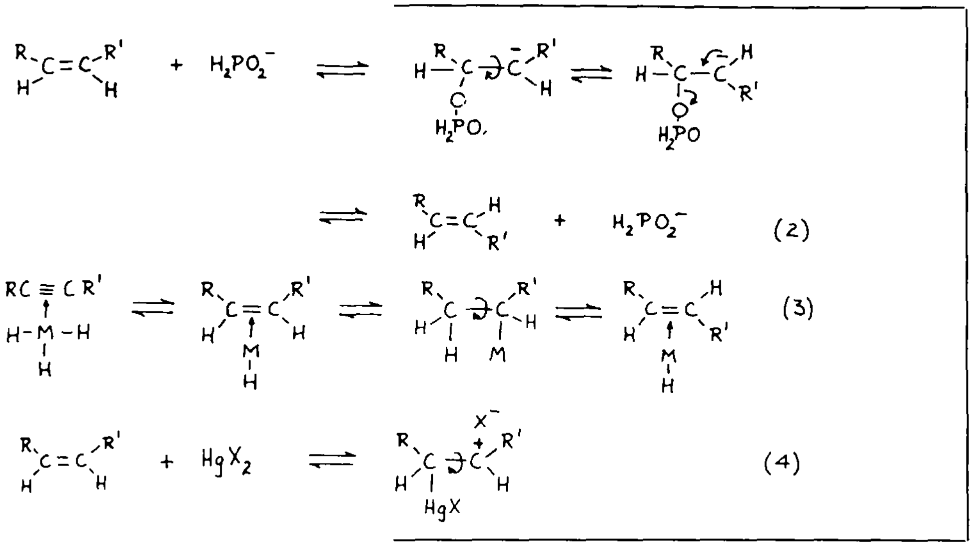
It will be noted from Table 1 that a little *trans*-1,2-diphenylethene was formed. Independent experiments have shown that most of this *trans* isomer is the result of rotation about the double-bond of the first-formed *cis* isomer and is not the result of its primary formation during reduction. Under the conditions used for reduction, a sample of pure *cis*-1,2-diphenylethene afforded a mixture of *cis*- and *trans*-1,2-diphenylethene in the ratio of 1:1.95 after 18 days. It seems clear the catalyst must be able to affect rotation about the double-bond and yet not lead to any significant further reduction to 1,2-diphenylethane. This observation was made even more interesting when it was found that, *in the absence of*

Table 2. Catalytic transfer reduction of some alkynes using modified catalysts

Alkyne	Catalyst[1] Ratio Pd : X)	Reaction Time	Product alkene (% yield)[2]
1,2-Diphenylethyne	Pd/Hg (0:0.5)	3hr 40 min	cis-1,2-diphenylethene (86)
	Pd/Pb (1:0.5)	2hr 40 min	cis-1,2-diphenylethene (85)
Phenylethyne	Pd/Hg (1:0.4)	2hr 30 min	phenylethene (styrene ; 92)*
Methyl stearolate	Pd/Pb (1:0.5)	19hr 35 min	methyl oleate (97)*
1-Ethynyl-1-cyclohexene	Pd/Hg (1:0.4)	1hr 30 min	1-ethenyl-1-cyclohexene (81)*
1-Ethynylcyclohexanol	Pd/Pb (1:1)	4hr 30 min	1-ethenylcyclohexanol (97)*
1-Phenylpropyne	Pd/Hg (1:0.3)	1hr 45 min	1-phenylpropene (76)
	Pd/Pb (1:0.7)	3hr 40 min	1-phenylpropene (78)
3-p-Nitrobenzoyl-oxypropyne	Pd/Pb (1:1)	30 min	3-p-aminobenzoyloxypropene (70)

[1] Catalyst prepared from commercial 10% Pd/C (w/w) by adding the requisite molar proportion of modifying metal (X = Pb or Hg). Molar ratio of Pd to X is given in parentheses.

[2] Isolated yields of product alkenes, except in those cases marked by an asterisk where the yield is based on gc results by direct comparison with authentic materials. All reactions were carried out at room temperature.



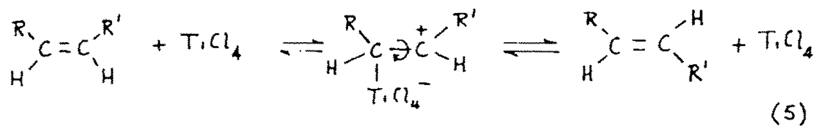
hydrogen donor, the catalyst did not give any significant conversion of *cis* to *trans* isomer. Such a result suggests either that the donor must be able to bond to the *cis*-alkene and allow rotation as shown in equation (2) or that addition of hydrogen to alkyne and abstraction of hydrogen from alkene is an equilibrium process, as illustrated in reaction (3). Interconversion of *cis*- and *trans*-alkenes is a well-documented process.[12] Many reagents afford equilibrium mixtures of the two alkenes rather than a specific interconversion and the conversions observed in this work appear to be other such cases. The equilibration of *cis*- and *trans*-alkenes could be effected rapidly through use of either $TiCl_4$ or mercury(II) trifluoromethylsulphonate, reagents which have not been used previously for this purpose. It is known that Hg(II) salts add to double- or triple-bonds, usually followed by nucleophilic attack of the counter ion[10](X^-) as shown in reaction(4). In the case of the poorly nucleophilic trifluoromethylsulphonate anion,[11] reaction (4) becomes reversible with the addition compound existing as an ion pair and allowing rotation about the centre C-C bond. The strongly electrophilic $TiCl_4$ affords no encounter ion but allows similar rotation, as in reaction (5). Both $TiCl_4$ and $Hg(CF_3SO_3)_2$ caused rapid equilibration of *cis*-alkenes to a mixture of *cis*- and *trans*-alkenes. For methyl oleate this equilibrium mixture was approximately in a 1:3 ratio of *cis* to *trans* isomers but for 1,2-diphenylethene, the *cis* isomer was converted almost entirely to *trans*.

The range of alkynes listed in Table 2 was chosen to illustrate the specificity and stereoselectivity that could be obtained using mercury- or lead-modified palladium catalysts. The terminal alkyne, phenylethyne, was reduced to phenylethene (styrene) in 92% yield and the disubstituted aliphatic alkyne, methyl stearolate, was reduced to methyl oleate in 97% yield. The conjugated ene-yne, 1-ethynyl-1-cyclohexene was reduced to the conjugated diene, 1-ethenyl-1-cyclohexene. In the last two examples, where migration of the double-bond might occur, none was observed thereby confirming the specificity of the reduction.

Under the conditions of catalytic transfer reduction described here, a nitro group is reduced more readily than an alkyne. Thus, 3-p-nitrobenzoyloxypropyne gave initially 3-p-aminobenzoyloxypropyne and then 3-p-aminobenzoyloxypropene. No cleavage of this normally labile C–O bond was observed.

Solvents

In most of the experiments, tetrahydrofuran was used as solvent. Other solvents had considerable effects on the rate and specificity of reduction. Thus, ethanol, toluene and petroleum ether tended to slow the reduction whilst acetone, ethylacetate and dioxan increased the rate of reaction



(5)

EXPERIMENTAL

Analysis of reaction products was carried out by GLC, ^{1}H-NMR, and MS, using authentic materials as standards in all cases.

Preparation of modified catalysts

In a typical experiment, commercially available (Engelhard) 10% Pd/C catalyst (0.053 g) was stirred vigorously in a solution of mercury(II) acetate (0.0793 g) and a solution of sodium tetrahydroborate (0.38 g) in water (10 ml) was added dropwise at room temperature. The mixture was stirred for 1 hr and then filtered. The residue was washed well with water (150 ml) and dried in a desiccator to give a catalyst with a molar ratio of Pd to Hg of 1.0:0.5. Other metal-modified catalysts were prepared similarly but, except for mercury, were dried in an oven at 50°. All catalysts were prepared from 10% Pd-on-charcoal.

Transfer reduction

In a typical experiment, methyl stearolate (0.147 g) was dissolved in tetrahydrofuran (5 ml). To this solution was added a solution of sodium phosphinate (0.88 g) in water (5 ml) and Pb-modified Pd/C catalyst (0.054 g) (ratio Pb to Pd = 0.5:1). The mixture was stirred for 19 hr 35 min at room temperature. The course of reaction was monitored by GLC. The catalyst was filtered and washed with fresh tetrahydrofuran. The filtrate and combined washings were dried ($MgSO_4$) and evaporated to yield methyl oleate (138 mg; pure by GLC, MS, ^{1}H-NMR: 87% yield of isolated product).

Other transfer reductions were carried out similarly. Reaction times varied with the nature of the alkyne and the degree of catalyst modification

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