Allylic Substitution using Heterogeneous Palladium Catalysts

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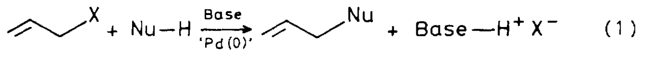
Allylic substitution of the acetoxy group of allylic acetates by various nucleophiles is catalysed by heterogeneous palladium catalysts in the presence of triphenylphosphine.

Nucleophilic allylic substitution reactions using various nucleophiles in the presence of homogeneous palladium(0) catalysts are well known, important synthetic reactions.[1] Most commonly, these reactions use homogeneous catalysts such as tetrakis(triphenylphosphine)palladium(0). Palladium(0) ligated by phosphinated polystyrene and phosphi-

Table 1. Effect of addition of triphenylphosphine on allylic substitution of allyl acetate by diethylamine catalysed by heterogeneous palladium catalysts.[a]

Yield (%)	Time/ h	Catalyst	PPh_3/Pd (mmol/mg atom)	Substrate/Pd (mmol/mg atom)
0	24	Pd/C	0	200
0	24	PS-Sib-Pd[b]	0	200
46	4	Pd/C	5	200
52	4	PS-Sib-Pd[b]	5	200
82	2	Pd/C	10	200
100	2	PS-Sib-Pd[b]	10	200
98	1	Pd/C	25	200

[a] Reactions were carried out using 2.5 mmol of allyl acetate and 5 mmol of diethylamine in 5 ml of toluene at 50 °C with analysis of the reaction products by gas chromatography. [b] Prepared as described in ref. 5 from polystyrylphenyl(trimethylsilyl)methyllithium and (cyclo-octadiene)palladium chloride.



X = $-O_2CMe$ Nu—H = R_2N-H
$-OPh$ $(CO_2Et)_2CH-H$
$-OCF(CF_3)_2$ $(MeCO)_2CH-H$

nated silica have also been used in some cases to advantage.[2,3] However, heterogeneous palladium catalysts such as Pd/C are generally not useful for this reaction although there have been isolated reports of highly dispersed palladium crystallites which have catalytic activity like that of $(Ph_3P)_4Pd$.[4,5] In this communication, we describe an alternative to these catalysts, namely, the use of heterogeneous palladium catalysts and catalytic amounts of triphenylphosphine.

The dramatic effect of adding triphenylphosphine to suspensions of Pd/C, allyl acetate, and amines to promote the general reaction shown by equation (1) is shown by the data in Table 1. We have used two different heterogeneous palladium catalysts; commercially available 1% Pd/C and Pd/polystyrene (PS-Sib-Pd) prepared from lithiated polystyrene and solutions of palladium(II) chloride.[5] The catalysts used in these reactions are readily recyclable at least 10 times. For example, after a series of ten reactions in which the allyl acetate:Pd ratio was 100:1, PS-Sib-Pd was still able to quantitatively convert allyl acetate and diethylamine into allyldiethylamine without any noticeable diminution of activity. As can be seen from the data in Table 2, a variety of nucleophiles work in this reaction. These reactions generally parallel the chemistry of the homogeneous $(Ph_3P)_4Pd$ solutions. However, reactions using an equivalent amount of the homogeneous palladium catalysts are at least an order of magnitude faster. This is not unexpected considering that the heterogeneous palladium catalysts consist of Pd crystallites, most of whose Pd atoms would not be available for reaction.

We have not yet been successful in determining if the catalysts in these reactions are really heterogeneous or if they are actually homogeneous. While it is possible that we are observing the chemistry of a phosphine ligated heterogeneous catalyst, our results are more likely to be due to triphenylphosphine leaching small amounts of palladium(0) from the palladium crystallites of these palladium(0) catalysts. However, if the latter case is true, the palladium species formed are evidently quite reactive. Examination of the residue obtained when these reaction solutions are concentrated failed to detect any palladium (<4 p.p.m. of Pd present in solution could have been detected in these analyses).

Table 2. Allylic substitutions using various substrates and various nucleophiles.[a]

Substrate	Nucleophile (Nu–H)	Yield[b] (%)	Substrate/Pd (mmol/mg atom)	Time/ h	Temperature/ °C	PPh_3/Pd (mmol/mg atom)	Solvent
$CH_2=CHCH_2OCF(CF_3)_2$	Cyclo-$C_5H_{10}N-H$	94 (7)[c]	200	1	25	2	THF[f]
$CH_2=CHCH_2OCOMe$	Cyclo-$C_5H_{10}N-H$	84 (23)[c]	200	0.5	65	2	THF
$CH_2=CHCH_2OCOMe$	Ph(Me)N–H	96	300	2	65	3	PhMe
$CH_2=CHCH_2OCOMe$	$(CO_2Et)_2CH-H$[d]	55 (21)[c]	1520	24	65	3	THF
$CH_2=CHCH_2OCOMe$	$(MeCO)_2CH-H$[d]	57 (40)[c]	1520	24	65	3	THF
$CH_2=CHCH_2OPh$	$(MeCO)_2CH-H$[d]	96[e]	2000	12	65	3	THF

[a] Substitution reactions were run under nitrogen on 2—40 mmol scales in pre-dried solvents using magnetic stirring. Products were characterized by i.r. and n.m.r. spectroscopy and compared with authentic materials using g.l.c. [b] Isolated yields of distilled product using PS-Sib-Pd as a catalyst except where indicated. [c] 1% Pd/C was used as the palladium catalyst. [d] An equivalent of triethylamine was added as a base. [e] Yield determined by gas chromatography. [f] THF = tetrahydrofuran.

Control experiments showed that allyl acetate does not react at a significant rate under our reaction conditions either alone, with only the heterogeneous palladium catalysts present, or with only triphenylphosphine present to form allyldiethylamine. Both triphenylphosphine and a palladium catalyst thus must be present for reaction (1) to occur. Diethylamine or some other nucleophile must also be present for the allyl acetate to react. This eliminates the possibility that palladium was catalysing a two step reaction involving first phosphonium salt formation followed by a second nucleophilic displacement of a triarylphosphine. Addition of triphenylphosphine does not promote all types of catalytic activity of these heterogeneous palladium catalysts. For example, hydrogenation of alkenes by these catalysts is strongly inhibited by the addition of trace amounts of triphenylphosphine.

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