SHORT PAPER

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Rapid and efficient palladium catalysed reduction of aryl halides by triethylsilane under microwave irradiation[†]

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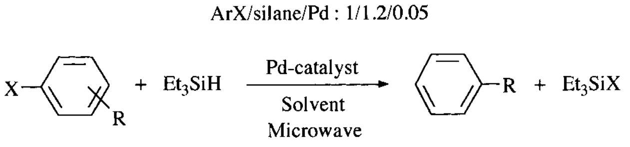
Triethylsilane in presence of catalytic amount of palladium chloride is an efficient and selective system for reductive dehalogenation of aryl halides under microwave irradiation.

Various procedures and reagents have been described for reductive dehalogenation.[1] Among them organotin hydrides react with many types of organic compounds. However, organotin compounds are highly toxic and difficult to remove from the reaction product. The silicon hydrides which are non toxic and stable compounds[2] can be considered as an alternative and effective reducing reagents,[3] in presence of an appropriate transition-metal complex,[4] despite their low ability to donate hydrogen atoms.[5] This combination is very attractive because of the ready insertion of the transition metal in the Si–H bond.

We have recently[6] described the use of palladium (II) dichlorobis (triphenylphosphine) as an air stable precursor of palladium (0) (bis-triphenylphosphine) in the Heck reaction. The complex of palladium was reduced *in situ* by triethylsilane. We observed that an excess of triethylsilane reduced the aryl halide substrate. The same observation was made during the Arbuzov type phosphonation of aryl halides[7] under microwave irradiation.[8] This reduction reaction of an aromatic halide can be of synthetic interest and is also useful for destruction of highly toxic polyhalogenated aromatic hydrocarbons (*i.e* PCBs).[9]

The use of microwave for activation of homogeneous transition metal catalyst is recent[8] and it is not reported in reduction by silanes.

We report herein a new simple, efficient and selective dehalogenation method of aryl halides using a silicon hydride and palladium catalyst in a solvent under microwave irradiation (Scheme 1).



Scheme 1

The results using triethylsilane in presence of catalytic amount of palladium dichloride were summarised in Table 1. Aryl iodides are quantitatively reduced in acetonitrile or ethanol after only 7 minutes of irradiation at 490 W (entries 1, 2 and 3). In a blank experiment, without palladium, no reaction was observed in the same conditions. 4-Bromoanisole in THF gave only 21% (entry 4), whilst 90% and 95% of dehalogenated product were achieved, respectively, in acetonitrile and triethylsilane as solvent (entries 5 and 6). The low yield obtained in THF is due to the small dielectric constant value of this solvent. Aryl chlorides react moderately and no reaction was observed with aryl fluoride (entry 11). This method tolerates the presence of different functions such as ketone, ester or nitro groups.

Table 1 Catalyst: $PdCl_2$

Entry	X, R	Solvent[a]	Irradiation (W)	Time (min)	Yields[b] (%)
1	I, 4–OMe	MeCN	490	7	>95[c]
2	I, 4–OMe	EtOH	300	7	>95[c]
3	I, 3–COOMe	MeCN	490	7	>95[c]
4	Br, 4–OMe	THF	490	7	21
5	Br, 4–OMe	MeCN	490	7	90
6	Br, 4–OMe	$HSiEt_3$	560	8	95
7	Br, 4–OH	MeCN	490	7	67
8	Br, 4–COMe	MeCN	490	8	95
9	Cl, 3–OMe	MeCN	490	7	68
10	Cl, 4–NO_2	MeCN	490	10	41
11	F, 4–CO_2H	MeCN	490	10	d

1 mmol of aryl halide, 1.5 mmol (1.5 eq) of Et_3SiH in 2 ml of solvent and 5 % molar of catalyst under argon; [a]dry solvents; [b]GC analysis using toluene as internal standard; [c]confirmed by ^1H and ^{13}C NMR; [d]no reaction.

The results reported in Table-2 show that the yields with the complexes [$(PPh_3)_2PdCl_2$ (A)] and [$P(o\text{-}tol_3)]_2PdCl_2$ (B)] are less important than those obtained with $PdCl_2$. The phosphines stabilising the palladium zero are unfavourable in this reduction.

Table 2 Catalysts: $(PPh_3)_2PdCl_2$ (A) or $[P(o\text{-}tol_3)]_2PdCl_2$ (B)

Entry	catalyst	X, R	Solvent[a]	Irradiation (W)	Time (min)	Yields[b] (%)
1	A	Br, 4-OMe	MeCN	420	8	c
2	A	I, 4-OMe	$HSiEt_3$	420	7	65
3	A	I, 4-OH	MeCN	560	7	14
4	B	I, 4-OMe	MeCN	500	7	50

1mmol of aryl halide, 1.5 mmol (1.5 eq) of Et_3SiH in 2 ml of solvent and 5–10 % molar of catalyst under argon; [a]dry solvents; [b]GC analysis using toluene as internal standard; [c]no reaction.

We have studied the influence of the silane on the reduction of 4-iodoanisole catalysed by palladium chloride (Scheme 2). Polymethylhydrosiloxane (PMHS),[10] is a non toxic, stable and commercially available polymer containing Si–H bond and the residues of its reaction are non hazardous. The results are reported in Table 3. PMHS which is insoluble in acetonitrile and slightly soluble in DMF (entries 2 and 4) gave poor yields (0 and 15% respectively). In ethanol (entry 3), at a lower microwave power, the yield was better than that in DMF. The soluble silane diphenylsilane (Ph_2SiH_2) is less efficient (32%) than triethylsilane.

Selectivity in the reduction by triethylsilane catalysed by palladium chloride was then tested in the reaction of several substrates, with two different functions. The results (Table 4) show that an aryl iodide is quantitatively reduced in presence

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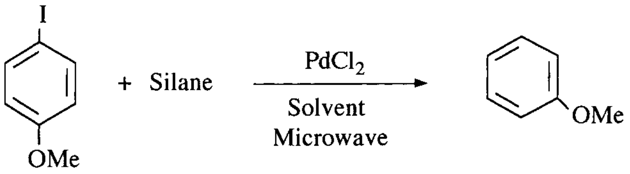
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 2

Table 3 Effect of nature of the silane

Entry	Silane	Solvent	Conditions	Yield[b] (%)
1	Et_3SiH	MeCN	490W / 8min	>95
2	PMHS[a]	MeCN	490W / 8min	0[c]
3	PMHS	EtOH (95%)	140W / 8min	47
4	PMHS	DMF	590W / 7min	15
5	Ph_2SiH_2	MeCN	490W / 8min	32

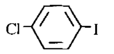
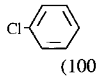
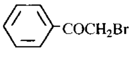
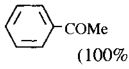
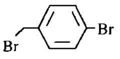
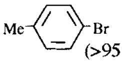
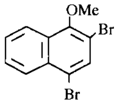
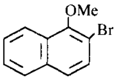
ArX/silane/Pd : 1/1.2/0.05

[a]Polymethylhydrosiloxane, [b]GC yields, [c]no reaction (PMHS is not soluble in MeCN).

of an aryl chloride (entry 1) and a bromoketone can be dehalogenated quantitatively yielding the parent carbonyl compound (entry 2). Benzyl bromide is selectively reduced in presence of an aryl bromide (entry 3). Finally, it is possible to reduce selectively, in the same molecule, one of two different bromides (entry 4).

This method was also applied to reduce acyl chlorides into aldehydes. We have obtained 48% yield of benzaldehyde from benzoyl chloride after irradiation at 490W during 8 minutes. This result is better than the one obtained by Citron (31%)[11] using Et_3SiH/Pd–C system. The reaction of 2, iodobenzoyl chloride, gave exclusively the reductive-decarbonylation product (iodobenzene). This last result was attributed to the preferential oxidative insertion taking place in the C–Cl bond of acid chloride.

Table 4 Reduction of different halides

Entry	Substrate	Conditions	Major products
1		490 W, 7 min	 (100%)
2		490 W, 9 min	 (100%)
3		490 W, 10 min	 (>95%)
4		490 W, 8 min	 (>95%)

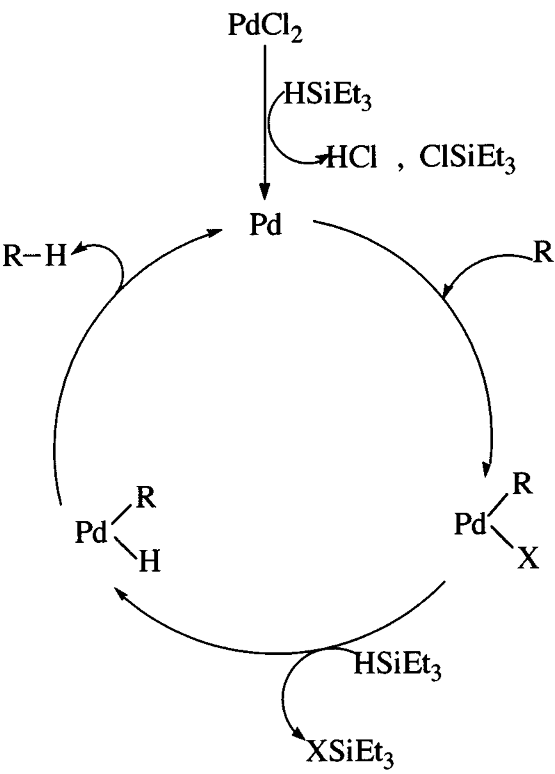
Substrate/Et_3SiH/Pd : 1/1/0.05

We propose the mechanism outlined in the scheme for the reduction of aryl halides by triethylsilane in presence of palladium chloride in acetonitrile.

In conclusion triethylsilane in presence of catalytic amount of palladium chloride is an efficient and selective system for reductive dehalogenation of aryl halides under microwave irradiation.

Experimental

Proton ^1H and ^{13}C NMR (reference from internal Me_4Si) were recorded on a Brücker AC 250 instrument from solution in $CDCl_3$. FT IR spectra were recorded on a Perkin-Elmer 16 PC spectrometer. GC yields were obtained by a Shimadzu GC-8A apparatus fitted with an OV17 column and a catharometer detector which is connected to a Spectra Physics integrator-recorder. Microwave irradiations were carried out in a Toshiba microwave oven ER 7620 at 2450 MHz. All reactions were done in a Teflon Savilex autoclave under argon atmosphere. Solvents were dried and degassed before use.



Scheme 3 Proposed mechanism for the palladium catalysed reduction of halides by the triethylsilane

Typical experiment: with 4-bromoanisole: A mixture of 4-bromoanisole (0.18 g, 1 mmol) and triethylsilane (0.24 ml, 1.5 mmol) in 2 ml of dried acetonitrile was added under argon atmosphere to $PdCl_2$ (9 mg, 0.05mmol) in an hermetically closed Teflon autoclave. 0.1 ml of toluene (internal standard) was added. Irradiation at 490 W during 2 minutes, 5 times 1 minutes at the same irradiation, the solution become black. After cooling, the mixture was filtered over Celite and analysed by GC. The products were isolated by a flash chromatography on short column of silica (cyclohexane/ethyl acetate) the solvent were eliminated by distillation under vacuum. The products were identified by NMR (^1H, ^{13}C) and mass spectroscopy.

The reactional mixtures before flash chromatography were analysed by G.C. The column used is a column OV17 (5%) of 1.5 m length, the oven temperature was programmed from 140 to 200°C (10°C per minute), injector and detector temperature were at 220°C, and the gas flow (H_2) was 40–50 ml/min Toluene was use as internal standard, with a retention times of anisole equal to 0.93 min.

The complexes of triphenylphosphine $[(PPh_3)_2PdCl_2$ (A)] and tri-o-tolylphosphine $[P(o\text{-}tol_3)]_2PdCl_2$ (B)]were obtained by complexation of the corresponding phosphines respectively with palladium chloride in DMF at room temperature.

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