Hydrogenation of Diphenylethyne Catalyzed by $PdCl_2$ in CH_2Cl_2 and Polyethylene Glycol

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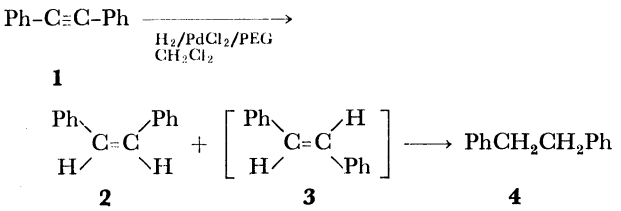
Synopsis. A practically homogeneous system of $PdCl_2$ in CH_2Cl_2 in the presence of polyethylene glycol catalyzed hydrogenation reactions of diphenylethyne (**1**) and *cis*-1,2-diphenylethene (**2**) to **2** and/or 1,2-diphenylethane (**4**). Under the conditions, the selectivity of the hydrogenation of **1** to **2** against that of **1** to **4** was excellent, compared to that using the Pd/C system.

Polyethylene glycol (PEG) is an excellent substitute of crown ether because of its low-price, low-toxicity, non-volatility, and solubility in both organic solvents and water (easily removable). It has been used as a co-solvent as described in our previous reports[1] and in others.[2]

Much data have been accumulated for the heterogeneous[3] and homogeneous[4] catalysts of hydrogenation. However, there has been no report on the hydrogenation catalyzed by $PdCl_2$ which is made soluble in organic solvents by means of some co-solvent(s). Although a few nucleophilic additions to alkenes and alkynes proceeding by initial formation of a double or triple bond-$PdCl_2$ complex were known,[5] there have been no reports on the hydrogenation of them catalyzed by $PdCl_2$. We describe here a novel homogeneous catalyst for the hydrogenation of diphenylethyne (**1**) and 1,2-diphenylethene (**2**) to the corresponding *cis*-olefin (**2**) and the saturated hydrocarbon (**4**), respectively. Good selectivity for the partial reduction of **1** to **2** was achieved. The reactions can be interrupted simply by washing with water. This makes it easy to maximize the selectivity. This is the first example of a homogeneous catalyst using a host-guest complex between PEG and palladium for the hydrogenation of alkynes and olefins.



Palladium chloride[6] placed in a round-bottomed flask was covered with H_2 gas. Into the flask was added a solution of diphenylethyne[6] (**1**) in CH_2Cl_2 or some other solvent(s) with or without PEG[7] through an injection needle. The resulting clear solution was stirred at 10 °C. The hydrogenation reactions were monitored by GLC by comparing with the authentic *cis*- and *trans*-1,2-diphenylethenes[6] (**2** and **3**) and 1,2-diphenylethane[7] (**4**). Palladium/C (10%) was employed for comparisons. The results are shown in Table 1. In the case of using PEG, the aliquots were washed with water to remove the PEG and the other water soluble components before the application on GLC. Conversion yields for **2** and **4** were calculated on the basis of the conversion of **1**, ignoring a trace of **3** (less than few %). Selectivity is represented by the ratio of [**2**]/[**4**]. Palladium black seemed not to be formed during the reaction.

Table 1 shows that $PdCl_2$ worked in EtOH similarly to the Pd/C, but the selectivity is lower than for the latter (runs No. 1 and 2 in Table 1). In CH_2Cl_2, Pd/C did not catalyze the reaction well and the conversion of **1** was low, while $PdCl_2$ worked well (runs No. 4—5).

Employment of PEG as a co-solvent in CH_2Cl_2 accelerated the reaction and gave higher selectivity (runs No. 3 and 7). A higher concentration of PEG #200, however, seems to lower the reaction rate and the selectivity (runs No. 3 and 6). The viscosity of the medium may affect these values.

Molecular weight of PEG affected both the rates and the selectivity: PEG #400 gave the highest selectivity (runs No. 6—9). This may be explained by the ease of the formation of complex between the PEG molecule and Pd^{2+} cation.[8] If the cation forms a complex bound with PEG too tightly, the complex formation might also cause the difficulty of contact between the catalyst and the substrate: Consequently, the reaction rates decreased when PEG of higher molecular weight was used.

The other solvents used gave less effective results (runs No. 10—13). PEG #200 did not give higher selectivity in $CHCl_3$.

Ethylene oxide-condensed pentaerythritols (PEO-8.3EO and PEO-15.8EO)[9] worked well as co-solvents as PEG (runs No. 14—15).

Similar catalytic hydrogenation occurred when *cis*-1,2-diphenylethene (**2**) was used as a substrate (see Table 2) under similar conditions to those used above. The conversion yields were quantitative, but the reaction rates were not satisfactory for the preparation of **4**.

Experimental

Diphenylethyne[6] (**1**), *cis*- and *trans*-1,2-diphenylethenes[6] (**2** and **3**), 1,2-diphenylethane[6] (**4**), $PdCl_2$,[6] and 10% Pd/C were purchased. Polyethylene glycols #200, #400, #600, and #1000 were purchased[7] and dried azeotropically (benzene) before use. EtOH (Mg) and CH_2Cl_2 (CaH_2) were dried over and distilled from the desiccant shown in the parentheses. GLC tests were performed on a Yanagimoto Yanaco G-80F (FID): 5% PEG-20 M on Gasport (60—80 mesh) in a stainless steel column (ϕ 2 mm×2.0 m); col. temp 160 °C, inj. temp 180 °C, carrier gas (N_2), 20.9 ml/min.

*Catalytic Hydrogenation of Diphenylethyne (**1**) or cis-1,2-Diphenylethene (**2**).* Palladium chloride or 10% Pd/C (final concentration: 0.94 mM) (1 M=1 mol dm^{-3}) was placed in a 50 ml-round-bottomed flask which was kept in a thermostated bath (10±0.5 °C) with a serum cap. The flask

Table 1. Hydrogenation of diphenylethyne (**1**) at 10 °C

Run No.	Solvent	Catalyst[a]	Co-solvent (M)	Conversion of **1** / %	Time / min	Conversion yield[b]/% **2**	Conversion yield[b]/% **4**	[2]/[4]
1	EtOH	Pd/C[c]	—[g]	60	8.5	75	25	3.00
				90	17	65	35	1.86
2		$PdCl_2$	—	60	9	55	45	1.22
				90	20	46	64	0.72
3	CH_2Cl_2		PEG #200[d] 1.0	60	50	71	29	2.45
				90	90	57	43	1.33
4		Pd/C	—	54	300	83	17	4.88
5		$PdCl_2$	—	60	83	67	33	2.03
				90	180	58	42	1.38
6			PEG #200 0.5	60	23	78	22	3.55
				90	45	62	38	1.63
7			PEG #400 0.5	60	31	80	20	4.00
				90	79	72	28	2.57
8			PEG #600 0.5	60	51	74	26	2.85
				90	120	57	43	1.33
9			PEG #1000 0.5	60	89	72	28	2.57
				81	180	57	43	1.33
10	Et_2		—	60	23	59	41	1.44
				90	54	40	60	0.67
11	Me_2CO		—	60	15	59	41	1.44
				90	64	25	75	0.33
12	$CHCl_3$		—	60	188	62	38	1.63
				66	240	62	38	1.63
13			PEG #200 1.0	60	225	50	50	1.00
				84	420	42	58	0.72
14	CH_2Cl_2		PEO-8.3EO[e] 1.0	60	28.5	69	31	2.23
				90	53	55	45	1.22
15			PEO-15.8EO[f] 1.0	60	31	68	32	2.13
				90	82	59	41	1·44

a) [**1**]: 10 mM; [cat.]: 0.94 mM. b) Trace amounts of **3** were also detected. c) Pd/C: 10% Palladium charcoal. d) PEG with mean mol. wt. of 200; others as written (Nakarai Chem. Co.). e) PEO-8.3EO: Pentaerythritol-8.3 ethylene oxide (Ref. 9). f) PEO-15.8EO: Pentaerythritol-15.8 ethylene oxide (Ref. 9). g) Not employed.

Table 2. Hydrogenation of *cis*-1,2-diphenylethene (**2**)

Run	Solvent	Catalyst[a]	PEG (M)	Conversion / %	Time / min	Conversion yield of **4**/%
1	CH_2Cl_2	Pd/C[b]	—	80	300	100
2	CH_2Cl_2	Pd/C	#200[c] 1.0	18	480	100
3	EtOH	Pd/C	—	90	100	82
4	CH_2Cl_2	$PdCl_2$	—	80	480	100
5	CH_2Cl_2	$PdCl_2$	#200 1.0	90	400	100
6	EtOH	$PdCl_2$	—	90	80	90
7	CH_2Cl_2	—	#200 1.0	0	120	—

a) [**1**]: 10 mM; [cat.]: 0.94 mM. b) Pd/C: 10% Palladium charcoal. c) PEG with mean mol. wt. of 200.

was evacuated with an aspirator through an injection needle which pierced the serum cap. A balloon containing H_2 gas was attached through another injection needle. The evacuation and the filling with H_2 gas were repeated three times. Finally, the needle with the aspirator was disconnected, while the needle with the balloon of H_2 gas was kept in place. A solution (25 ml) of diphenylethyne (**1**: 10 mM) or *cis*-1,2-diphenylethene (**2**: 40 mM) in CH_2Cl_2 or the other solvent(s) with/without PEG (1 M) was added into the flask through an injection needle. The resulting clear solution was stirred at 10 °C. The hydrogenation reactions were monitored by GLC, comparing with the authentic samples, *cis*- and *trans*-1,2-diphenylethenes (**2** and **3**) and/or 1,2-diphenylethane (**4**). Recovery of **1** and generation of **2**, **3**, and **4** were observed. Conversion yields for **2** and **4** were calculated on the basis of the conversion of **1**, ignoring the trace amounts of **3** (less than a few %). Selectivity of the hydrogenation is represented by the ratio of [**2**]/[**4**]. The results are summarized in Tables 1 and 2.

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9) PEO-*m*EO: Pentaerythritols condensed with *m* mol of ethylene oxide units (Prepared by Yokkaichi Synth. Ind.).