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EFFECTIVE HYDROGENATION OF CARBON-CARBON TRIPLE BONDS BY $NaBH_4/PdCl_2$ IN POLYETHYLENE GLYCOL/CH_2Cl_2: USEFULNESS OF PEG IN SYNTHETIC REACTIONS[1]

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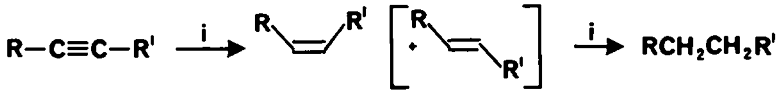
Abstract — The $NaBH_4$-$PdCl_2$-polyethylene glycol-CH_2Cl_2 system has been found to be effective for the hydrogenation of carbon-carbon triple bonds to the corresponding cis-alkenes.

Cyclic polyethers (crown ethers) attract keen interests of many investigators because of the rather high selectivity of the reactions by the activated anion species in the circumstances. Many interesting reactions were performed in crown ethers.

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[2] and in others:[3] Santaniello et al. have reported oxidation of benzylic bromides to the corresponding aldehydes by $K_2Cr_2O_7$ in PEG #400 at 110 °C (yields ∿ 85%);[3a] substitution of alkyl bromides to the corresponding R-X compounds by K-X (X = OAc, CN, I, and OPh) in PEG at 110 °C (yields 88 ∿ 94%);[3a] reduction of methyl ketones to the corresponding alcohols by $NaBH_4$ in PEG at 25 °C;[3a] hydrogenation of carboxylic esters to the corresponding primary alcohols by $NaBH_4$ in PEG #400 at 65 °C (10 h).[3b] Sukata also has reported an effective ether synthesis from an alcohol and an alkyl chloride by KOH or NaOH in PEG or dialkyl PEG (glymes) and aqueous MeOH at 30 - 70 °C.[3c]

Intending to find out new preparative organic reactions using PEG as a co-solvent, we have investigated several photochemical and dark reactions,[2] e.g., photochemical nucleophilic substitution reactions of anisole[2a-c] and o- and p-dimethoxybenzenes[2c-d] by ^-CN anion which was activated by PEG and also assisted by electron-transfer complex formation with dicyanobenzene; catalytic hydrogenation of acetylenic compounds by $H_2/PdCl_2$ in PEG/CH_2Cl_2;[2e-f] effective diazotization and Sandmeyer substitution reactions of arylamines.[2g] We have now found that selective hydrogenation of acetylenic triple bonds takes place with $NaBH_4$-$PdCl_2$ in PEG-CH_2Cl_2 systems,[4,5] providing the first example of the hydrogenation of acetylenes using $NaBH_4$ (Scheme 1).



1 **2** **3** **4**

a: R = R'= Ph
b: R = Ph, R'= H
c: R = Ph, R'= p-C_6H_4-CN
d: R = Et, R'= CH_2CO_2Me
e: R = R'= CO_2Me

Scheme 1. i, $NaBH_4$-$PdCl_2$ in PEG-CH_2Cl_2

$EtC{\equiv}CCH_2CH_2OH$ **5**

$EtCH{=}CHCH_2CH_2OH$ **6**, cis or trans

$Me[CH_2]_5OH$ **7**

Results and Discussion

With $PdCl_2$-PEG, all the five starting substrates examined (**1**: 10 mM) were consumed completely in an hour. The acetylenes (**1a** and **1c**) gave the cis-alkenes (**2a** and **2c**) as the major products, and only minor yields of the saturated compounds (**4a** and **4c**). At the most, only traces of the trans-alkenes (**3a** and **3c**) were formed. Reactions were faster with PEG, and the PEG-$PdCl_2$ combination led to higher selectivity for formation of **2** and **4** (see Table 1).

Hydrogenation of phenylacetylene (**1b**) under similar conditions gave similar results, except, of course, for the cis-trans-isomerisation.

Both the selectivity for formation of **2** and **4** and the yields were much improved, compared with our previous results for catalytic hydrogenation using the similar $H_2/PdCl_2$/PEG system (**1a**: [**2**]/[**4**] = 3.55).[2e-f]

Amounts of $NaBH_4$ affected the selectivity significantly: 20 ∿ 30 mM of the hydride was optimal for **1a**. Neither the aromatic nucleus nor the cyano group were hydrogenated. No change was observed by the addition orders (A-C) examined except the method D. Incubation of $NaBH_4$ and $PdCl_2$ in PEG/CH_2Cl_2 decreased both the reaction rate and the yield of **2**.

Hydrogenation of the acetylenic esters (**1d** and **1e**). From the unconjugated ester (**1d**),[6] similar results were obtained to those of **1a** and **1c**. The alcoholic products (**5** - **7**) were not produced from **1d** with the $PdCl_2/NaBH_4$/PEG/CH_2Cl_2 system, in contrast with Santaniello's results with $NaBH_4$-PEG systems.[3b] When $NaBH_4$ was dissolved in PEG-CH_2Cl_2 and the solution left for >2 h before mixing with the substrate (**1d**) and $PdCl_2$, the main reaction was hydrogenolysis of the esters. These results can be explained by the formation of the reagent $NaBH_n(OR)_{4-n}$;[3b,7] $PdCl_2$ seems to suppress hydrogenolysis of **1** - **4** to the alcoholic compounds. $PdCl_2$ was more effective than Pd/C with respect to both rate and selectivity (see Table 2).

The conjugated ester dimethyl acetylenedicarboxylate (**1e**) gave much complex results; various ratios of cis- and trans-alkenes together various amounts of the saturated ester were obtained. No alcoholic products were produced from **1e** (see Table 3). For the production of cis-olefin (**2**), PdI_2 was more effective than $PdCl_2$, especially under the lower concentration of $NaBH_4$. Both complex formation by $NaBH_4$-PEG and by $PdCl_2$- PEG seems to be unfavorable.

The $PdCl_2$ apparently dissolved completely in the PEG used, but it is not clear whether or not Pd-black was generated.[8] Generation of Pd° by the reaction of $PdCl_2$ and $NaBH_4$ seems to be unfavorable for this hydrogenation.

There have been a few reports on the hydrogenation of conjugated olefinic lactones[9] and esters.[10] Brown et al. reported the catalytic hydrogenation of alkenes by hydrogen generated from $NaBH_4$ in the presence of a mineral acid.[11] However, the mechanism seems to be different from that for the present system, which contained no acid. Results under the method D supported the conclusion, also.

Some examples have been shown by Goto et al. that the presence of trace amounts of heavy metal ions affects the reaction pathways for the reaction of $NaBH_4$ on the bromo ketones.[4]

$LiAlH_4$ is well known to reduce triple bonds in tetrahydrofuran or diglyme to give the corresponding trans-alkenes,[12] but the present system has the advantages of faster rates and higher selectivity, together with the easier handling of $NaBH_4$ than $LiAlH_4$. Also cis-alkenes are obtained free from the trans-isomers.

Experimental

All the acetylenes (**1a** ∿ **e**) and the authentic samples (**2a** - **c**, **2e**, **3a** - **c**, **3e**, **4a** - **e**, and **5** - **7**) used were commercially available. The cis- and trans-hexenoates (**2d** and **3d**) were prepared as a 10:1 mixture by esterification of commercially available acids, and the structures were identified by NMR comparison with the corresponding cis-alcohol (**6**).

General Methods for the Hydrogenation. A: A solution of diphenylacetylene (**1a**), phenylacetylene (**1b**), p-cyanodiphenylacetylene (**1c**), the unconjugated ester methyl 3-hexynoate[6] (**1d**), or dimethyl acetylenedicarboxylate (**1e**) (10 mM) either in PEG #200 (average mol. wt. = 200; Nakarai Chem. Co.) (1 mM ; dried azeotropically with benzene) diluted with dry CH_2Cl_2 to 25 ml, or in EtOH (25 ml) alone, was added to solid $PdCl_2$ (final conc. 1.13 mM) and $NaBH_4$ (200 mM). Four other addition orders (B-E) were examined: B: An incubated solution (10 °C, 2 h) of $NaBH_4$ in PEG/CH_2Cl_2 was added to **1** and $PdCl_2$; C: An incubated solution (10 °C, 2 h) of **1** and $PdCl_2$ in PEG/CH_2Cl_2 was added to solid $NaBH_4$; D: A solution of **1** was added to an incubated solution (10 °C, 2 h) of $NaBH_4$ and $PdCl_2$ in PEG/CH_2Cl_2; E: An incubated solution of $PdCl_2$ in PEG/CH_2Cl_2 was added to solid $NaBH_4$ and **1**. The resulting clear solution was stirred at 10 °C (1 atm). Samples were withdrawn at intervals and, for the reactions involving PEG, washed with 1 M HCl and water. The products were identified by g.l.c. comparison with authentic samples. As comparisons 10% Pd/C and PdI_2 were used instead of $PdCl_2$ in the PEG-CH_2Cl_2 system. The results are shown in Table 1 - 3.

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1 M = 1 mol dm^{-3}.

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Table 1. Hydrogenation of Arylacetylenes (1; 10 mM) with $NaBH_4/PdCl_2/PEG/CH_2Cl_2$ at 10 °C.

1	Solv.[a]	Method[h]	$NaBH_4$ (mM)	$PdCl_2$ (mM)	PEG #200 (M)	Consump. of 1 (%)	Time (min)	Yield (%)[c]			[2]/[4]
								2	3	4	
1a	A	A	200	1.13	1.0	100	30	91	t[e]	9	10.1
	A	A	200	--	1.0	0	60	n.d.[d]	n.d.	n.d.	--[f]
	A	A	200	1.13	--	60	120	75	n.d.	25	3.0
	A	A	200	1.13[b]	1.0	1[g]	180	66	n.d.	33	2.0
	B	A	200	1.13	--	40[g]	30	85	t	15	5.7
	B	A	200	1.13[b]	--	4[g]	120	90	t	10	9.0
	A	A	10	1.13	1.0	84	240	98	n.d.	n.d.	—
	A	B	20	1.13	1.0	99	360	96	n.d.	n.d.	—
	A	C	30	1.13	1.0	94	360	99	t	n.d.	—
	A	D	30	1.13	1.0	51	200	23	n.d.	n.d.	—
1b	A	A	80	1.13	1.0	100	10	77	—	8	9.6
	A	A	80	--	1.0	7[g]	60	t	—	n.d.	--
	A	A	80	1.13	--	40[g]	180	100	—	n.d.	--
	A	A	80	1.13[b]	1.0	100	360	81	—	18	4.5
	B	A	80	1.13	--	100	30	52	—	12	4.3
	B	A	80	1.13[b]	--	100	110	25	—	7	3.6
1c	A	A	200	1.13	1.0	100	20	85	t	15	5.7
	A	A	200	1.13	--	35[g]	20 h	97	t	3	32
	A	A	200	--	1.0	5[g]	18 h	98	—	t	--
	A	A	200	1.13[b]	1.0	5[g]	18 h	89	t	10	8.9
	B	A	200	1.13	--	80	70	11	—	17	0.7
	B	A	200	1.13[b]	--	85	120	13	—	20	0.7

a) A: CH_2Cl_2; B: EtOH. b) Pd/C. c) Conversion yields based on the consumption of 1. d) n.d.: not detected. e) t: trace. f) no data. g) Incomplete reaction. h) Addition orders; A: A solution of 1 in PEG/CH_2Cl_2 was added to solid $NaBH_4$ and $PdCl_2$; B: An incubated solution of $NaBH_4$ in PEG/CH_2Cl_2 was added to 1 and $PdCl_2$; C: An incubated solution of 1 and $PdCl_2$ in PEG/CH_2Cl_2 was added to solid $NaBH_4$; D: A solution of **1** was added to an incubated solution of $NaBH_4$ and $PdCl_2$ in PEG/CH_2Cl_2; (E) Onto a mixture of $NaBH_4$ (S) and 1 (L) added an incubated solution of $PdCl_2$ in PEG/CH_2Cl_2.

Table 2. Hydrogenation of An Acetylenic Ester (**1d**; 10 mM) with $NaBH_4/PdCl_2/PEG/CH_2Cl_2$ at 10 °C.

Solv.[a]	Method[h]	$NaBH_4$ (mM)	$PdCl_2$ (mM)	PEG #200 (M)	Consump. of **1d** (%)	Time (min)	Yield (%)[c] 2	3	4	[2]/[4]
A	A	80	1.13	1.0	100	60	86	t[e]	7	12.3
A	A	50	1.13	1.0	100	180	72	t	6	12.0
A	A	80	--	1.0	58	360	14	n.d.[d]	n.d.	--[f]
					98	23 h	21	n.d.	n.d.	--
A	A	80	1.13	--	95	360	73	2	4	18.3
					100	23 h	72	3	5	14.4
A	A	80	1.13[b]	1.0	70	480	20	t	t	--
					100	23 h	38	12	2	19.0
B	A	80	1.13	--	94	63	38	8	t	--
					100	120	24	8	t	--
B	A	80	1.13[b]	--	99	43	53	12	n.d.	--
					100	135	41	26	n.d.	--
A	B	80	1.13	1.0	100	15	15	n.d.	t	--

a - h) See footnotes in Table 1.

Table 3. Hydrogenation of Dimethyl Acetylenedicarboxylate (**1e**; 10 mM) with $NaBH_4/PdX_2/PEG/CH_2Cl_2$.

Method[a]	Temp. (°C)	$NaBH_4$ (mM)	$PdCl_2$ (mM)	Consump. of 1e (%)	Time (min)	Yield (%)[c] 2	3	4	[2]/[4]	[2]/[3]
A	10	10	1.13	100	5	10	27	44	0.2	0.37
A	10	10	1.13[b]	100	15	19	20	25	0.76	0.95
A	10	5	1.13	93	75	23	18	17	1.35	1.28
B	10	10	1.13	100	10	24	18	22	1.09	1.33
B	10	10	1.13	97	390	2.1	1.5	5.2	0.40	1.40
C	10	10	1.13	100	5	20	23	35	0.57	0.87
C	10	10	1.13	100	45	27	19	20	1.35	1.42
D	10	10	1.13	42	240	5	19	6	0.83	0.26
E	10	10	1.13	100	10	9.5	15	21	0.45	0.63
A	10	10	—	100	20	8	32	33	0.24	0.25
B	10	10	—	100	30	9	36	27	0.33	0.25
A	0	10	1.13	100	10	16	22	41	0.39	0.73
B	0	10	1.13	100	120	28	17	23	1.22	1.65
C	0	10	1.13	100	30	30	23	26	1.15	1.30
C	10	10	5.6	100	5	14	16	57	0.25	0.88
E	10	10	5.6	100	10	7.5	9.5	15.5	0.48	0.79
C	20	5	1.13	99	240	25	21	16	1.56	1.19
C	20	5	5.6	99	240	39	13	10	3.9	3.00
C	20	5	5.6[b]	55	210	60	17	9	6.67	3.53

a, c) See footnotes h and c in Table 1, resp. b) PdI_2. d) Added after standing at 10 °C for 20 h.

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