Selective Reactions in Polyethylene Glycol. Hydrogenation of Acetylenes by $NaBH_4$–$PdCl_2$ in Polyethylene Glycol–Methylene Dichloride

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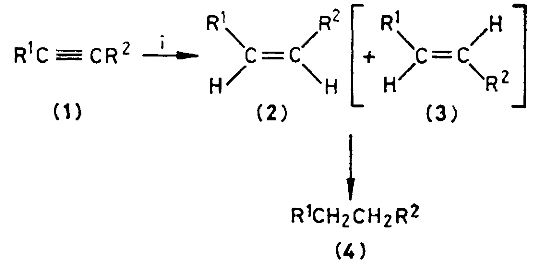
The $NaBH_4$–$PdCl_2$–polyethylene glycol–CH_2Cl_2 system has been found to be effective for the hydrogenation of acetylenic triple bonds to the corresponding *cis*-alkenes.

The properties of polyethylene glycol (PEG) make it an excellent substitute for crown ethers in many reactions, and its use as a co-solvent has been reported.[1,2] We have now found that selective hydrogenation of acetylenic triple bonds takes place with $NaBH_4$-$PdCl_2$ in PEG-CH_2Cl_2 systems,[3,4] providing the first example of the hydrogenation of acetylenes using $NaBH_4$ (Scheme 1).

A solution of diphenylacetylene (**1a**), phenylacetylene (**1b**), or the unconjugated ester methyl hex-3-ynoate[5] (**1c**) (10 mmol l^{-1}) either in PEG 200 (1 mol l^{-1}; 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. 0.94 mmol l^{-1}) and $NaBH_4$ (200 mmol l^{-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 Samples were withdrawn at intervals and, for the reactions involving PEG, washed with water. The products were identified by g.l.c. comparison with authentic samples.† As a comparison 10% Pd/C was used instead of $PdCl_2$ in the PEG–CH_2Cl_2 system. The results are in Table 1.



a; $R^1 = R^2 = Ph$
b; $R^1 = Ph, R^2 = H$
c; $R^1 = Et, R^2 = CH_2CO_2Me$

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

With $PdCl_2$–PEG, the starting materials (**1**) 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**). The alcoholic products (**5**)—(**7**) were not produced from (**1c**) with the $PdCl_2$ system, in contrast with Santaniello's results with $NaBH_4$–PEG systems.[2b] When $NaBH_4$ was dissolved in PEG–CH_2Cl_2 and the solution left for >2 h before mixing with the substrate (**1c**) and $PdCl_2$, the main reaction was hydrogenolysis of the esters. These results can be explained by the formation of the reagent $NaBH_n(OR)_{4-n}$;[2b,6] $PdCl_2$ 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. Hydrogenation of phenylacetylene

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

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

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

$MeO_2CC{\equiv}CCO_2Me$
(**8**)

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† (**2a, b**), (**3a**), (**4a**—**c**), and (**5**)—(**7**) were commercially available. (**2c**) and (**3d**) were prepared as a 10:1 mixture of *cis–trans*-isomers by esterification of commercially available acids, and were identified by n.m.r. comparison with the corresponding *cis*-alcohol (**6**).

Table 1. Hydrogenation of acetylenes (**1**) with $NaBH_4$–$PdCl_2$–PEG–CH_2Cl_2 at 10 °C.

Acetylene (10 mmol l^{-1})	Solvent[a]	$NaBH_4$/mmol l^{-1}	Catalyst/mmol l^{-1}		mol l^{-1} of PEG 200	% Consumption of (**1**)	Time/min	% Yield[c]			(**2**)/(**4**)
			$PdCl_2$	Pd/C				(**2**)	(**3**)	(**4**)	
(**1a**)	A	200	0.94	—[b]	1.0	100	30	91	t[e]	9	10.1
	A	200	—[b]	—	1.0	0	60	n.d.[d]	n.d.	n.d.	—[f]
	A	200	0.94	—	—	60	120	75	n.d.	25	3.0
	A	200	—	0.94	1.0	1[g]	180	66	n.d.	33	2.0
	B	200	0.94	—	—	40[g]	30	85	t	15	5.7
	B	200	—	0.94	—	4[g]	120	90	t	10	9.0
(**1b**)	A	80	0.94	—	1.0	100	10	77	—	8	9.6
	A	80	—	—	1.0	7[g]	60	t	—	n.d.	—
	A	80	0.94	—	—	40[g]	180	100	—	n.d.	—
	A	80	—	0.94	1.0	100	360	81	—	18	4.5
	B	80	0.94	—	—	100	30	52	—	12	4.3
	B	80	—	0.94	—	100	110	25	—	7	3.6
(**1c**)	A	80	0.94	—	1.0	100	60	86	t	7	12.3
	A	50	0.94	—	1.0	100	180	72	t	6	12.0
	A	80	—	—	1.0	58	360	14	n.d.	n.d.	—
						98	23 h	21	n.d.	n.d.	—
	A	80	0.94	—	—	95	360	73	2	4	18.3
						100	23 h	72	3	5	14.4
	A	80	—	0.94	1.0	70	480	20	t	t	—
						100	23 h	38	12	2	19.0
	B	80	0.94	—	—	94	63	38	8	t	—
						100	120	24	8	t	—
	B	80	—	0.94	—	99	43	53	12	n.d.	—
						100	135	41	26	n.d.	—
	A	80[h]	0.94	—	1.0	100	15	15	n.d.	t	—

[a] A: CH_2Cl_2; B: EtOH. [b] Not employed. [c] Conversion yields based on the consumption of (**1**). [d] n.d.: not detected. [e] t: trace. [f] No data. [g] Incomplete reaction. [h] $NaBH_4$–PEG–CH_2Cl_2 was added to $PdCl_2$ + (**1c**) after it had been left for 2 h at 10 °C.

(**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 $PdCl_2$–PEG–H_2 system [(**1a**): (**2**)/(**4**) = 3.55].[1]

The conjugated ester dimethyl acetylenedicarboxylate (**8**) gave irreproducible results; various ratios of *cis*- and *trans*-alkenes together various amounts of the saturated ester were obtained.[7]

The $PdCl_2$ apparently dissolved completely in the PEG used, but it is not clear whether or not Pd-black was generated.[8]

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.

$LiAlH_4$ 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.

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References

1 N. Suzuki, Y. Ayaguchi, and Y. Izawa, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3349; N. Suzuki, Y. Ayaguchi, K. Shimazu, T. Ito, and Y. Izawa, in A.C.S. Symposium Series, 'Crown Ethers and Phase Transfer Catalysis in Polymer Science,' eds. C. E. Carraher and L. Mathias, Plenum Press, New York, 1982; *Bull. Chem. Soc. Jpn.*, 1983, **56**, 304.

2 (a) E. Santaniello, A. Manzocchi, and P. Sozzani, *Tetrahedron Lett.*, 1979, 4581; E. Santaniello, P. Ferraboschi, and P. Sozzani, *J. Org. Chem.*, 1981, **46**, 4584; (c) K. Sukata, *J. Synth. Org. Chem. Jpn.*, 1981, **39**, 443.

3 Effects of a trace of Pb^{2+} on the reduction of α-bromoketones by $NaBH_4$ have been found; T. Goto and Y. Kishi, *J. Chem. Soc. Jpn.*, 1962, **83**, 1135; T. Kondo, H. Kondo, and T. Goto, *ibid.*, 1970, **91**, 470.

4 (a) T. Satoh, N. Mitsuo, M. Nishiki, K. Nanba, and S. Suzuki, *Chem. Lett.*, 1981, 1029; (b) T. Satoh, N. Mitsuo, M. Nishiki, Y. Inoue, and Y. Ooi, *Chem. Pharm. Bull.*, 1981, **29**, 1443; M. Nishiki, H. Miyataka, Y. Niino, N. Mitsuo, and T. Satoh, *Tetrahedron Lett.*, 1982, **23**, 193.

5 K. E. Schulte and W. Engelhardt, *Arch. Pharm.*, 1954, **287**, 495.

6 A. Hajós, 'Complex Hydride and Related Reducing Agents in Organic Synthesis,' Elsevier, Amsterdam, 1979, p. 61.

7 N. Suzuki, unpublished work.

8 T. W. Russell and D. M. Duncan, *J. Org. Chem.*, 1974, **39**, 3050.

9 D. Satoh and T. Hashimoto, *Chem. Pharm. Bull.*, 1976, **24**, 1950.

10 S. B. Kadin, *J. Org. Chem.*, 1966, **31**, 620.

11 H. C. Brown, K. Sivasankaran, and C. A. Brown, *J. Org. Chem.*, 1963, **28**, 214.

12 *E.g.*, L. H. Slaugh, *Tetrahedron*, 1966, **22**, 1741; E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *J. Am. Chem. Soc.*, 1967, **89**, 4245; B. B. Molloy and K. L. Hauser, *Chem. Commun.*, 1968, 1017; A. Claesson, *Acta Chem. Scand., Ser. B*, 1975, **29**, 609; M. Hojo, R. Masuda, and S. Takagi, *Synthesis*, 1978, 284.