"P-2 Nickel" Catalyst with Ethylenediamine, a Novel System for Highly Stereospecific Reduction of Alkynes to *cis*-Olefins

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Summary Borohydride-reduced nickel (P-2 Ni), used with ethylenediamine, is highly stereospecific for the hydrogenation of alkynes to pure olefins with *cis*:*trans* ratios as high as 200:1.

Reduction of nickel(II) acetate with sodium borohydride in ethanol yields a nearly colloidal non-magnetic black nickel catalyst, P-2 nickel, which is extremely sensitive to substrate structure in olefin hydrogenation.[1] Reduction of disubstituted alkynes with this catalyst results in high yields of the corresponding alkenes with *cis*:*trans* ratios of 30:1.[2] Thus, hex-3-yne gives 96% hex-3-ene (*cis*:*trans* 29:1).[2b]

Investigation of a series of amines[†] as catalyst modifiers[2c] showed ethylenediamine to be effective for the production of pure *cis*-alkenes. It can be readily removed from the products during work-up with neutral water washes. Thus, reduction of hex-3-yne with a large catalyst loading (40·0 mmol hex-3-yne, 5·0 mmol P-2 Ni) in ethanol containing ethylenediamine (1·0 ml, 16 mmol) yielded 95·1% hex-3-ene with a *cis*:*trans* ratio of 100:1. With a lower catalyst loading (200 mmol hex-3-yne, 10·0 mmol P-2 Ni, 32 mmol ethylenediamine), the *cis*:*trans* ratio was 200:1. Similar results were observed with 1-phenylpropyne (see Table).

Table

Stereospecific reduction of $R^1C{\equiv}CR^2$ *by* P-2 Ni-eda[a]

Substrate (mmol)	P-2Ni (mmol)	% Olefin[b]	*cis*:*trans*[b]	Total yield(%)
Hex-3-yne(40)	5·0	98	97:1	>95[b]
Hex-3-yne(200)	10·0	97	*ca.* 200:1	>95[b] (80)[c]
1-Phenylpropyne(100)	5·0	96	*ca.* 200:1	>95[b]
Hex-3-yn-1-ol(40)	5·0	98	>100:1	94[c]

[a] Amine used was 2—3 × molar amounts of catalyst. There is no evidence that this excess is required. [b] G.l.p.c. analysis. [c] Isolated yield.

[†] Quinoline, pyridine, ethylenediamine, piperidine, morpholine, and triethylamine.

The following procedure is representative. P-2 nickel was prepared[1] *via* borohydride reduction of $Ni(C_2H_3O_2)_2,4H_2O$ (1·25 g, 5·0 mmol). The reactor was purged with hydrogen and ethylenediamine (0·66 ml, 10 mmol) was added, followed by hex-3-yn-1-ol (3·92 g, 40·0 mmol). Hydrogen uptake was quantitative in 12 min and then virtually ceased. The reaction mixture was filteerd through 1/8 in. of activated carbon, diluted with water, and extracted with ether. The combined ether extracts were washed with water, dried, and evaporated under vacuum to yield *cis*-hex-3-en-1-ol[3a–c] (3·75 g, 94%), 3,5-dinitrobenzoate, m.p. 49° (lit. [3d] m.p. 49·5°).

Reductions were carried out at 20—25°, 1 atm. press, in a Brown[□] hydrogenator. G.l.p.c.[4] on Carbowax 6000 (10% on Chromosorb W, 6 ft × 0·1 in i.d.) showed 2% n-hexanol, no starting material, and no detectable ($<1\%$) *trans*.

In a similar manner, dodec-7-yn-1-ol was reduced to *cis*-dodec-7-en-1-ol (an immediate precursor of a sex pheromone of the cabbage looper moth).

P-2 nickel alone is sluggish toward double bonds of even moderate hindrance (*e.g.*, t-butylethylene); the presence of ethylenediamine results in a catalyst regeospecific for alkynes. Thus, P-2 nickel plus ethylenediamine presents a remarkably specific tool for conversion of alkynes into pure *cis*-alkenes.

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[1] H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, 1963, **85**, 1005; C. A. Brown and V. K. Ahuja, *J. Org. Chem.*, in the press.

[2] For a discussion of the selective hydrogenation of alkynes see (a) M. Freifelder, 'Practical Catalytic Hydrogenation,' Wiley-Interscience, New York, 1971, ch. VIII; (b) Although it is generally assumed that quinoline + lead poisoned $Pd/CaCO_3$ yields pure *cis*-olefins, in fact substantial amounts of *trans*-olefins have frequently been reported. Furthermore, the *cis* : *trans* ratio with various Pd catalysts is generally 20—40 : 1, see ref. 2a, p. 119; (c) Ref. 2a, ch. IV and pp. 99—109.

[3] (a) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1950, 873; (b) S. H. Harper and R. J. D. Smith, *ibid.*, 1955, 1512; (c) F. Sondhiemer, *ibid.*, 1950, 877, reports formation of substantial amounts of *trans*-hex-3-en-1-ol during hydrogenation over $Pd/CaCO_3$; (d) A. J. Clark and L. Crombie, *Chem. and Ind.*, 1957, 143.

[4] E. Honkanen, T. Horsio, M. Ohno, and A. Hatanaka, *Acta Chem. Scand.*, 1963, **17**, 2051.