Tetrahedron Letters No. 1, pp 15 - 16, 1976. Pergamon Press. Printed in Great Britain.

REDUCTION OF ALKYNES AND MONOSUBSTITUTED ALKENES WITH LITHIUM ALUMINUM HYDRIDE AND TITANIUM TETRACHLORIDE

P. W. Chum and Stanley E. Wilson*

Department of Chemistry, Oregon State University

Corvallis, OR 97331

(Received in USA 10 October 1975; received in UK for publication 20 November 1975)

A number of complexes containing titanium or zirconium are known to be effective in the reduction of multiple carbon-carbon bonds.[1] In some cases the complex acts as a reagent (if a hydride) and in other instances as a catalyst for hydrogenation. This communication reports results on the convenient reduction of alkynes and monosubstituted alkenes by a reagent generated *in situ* from the dropwise addition of titanium tetrachloride to an ethereal solution containing lithium aluminum hydride and the unsaturated hydrocarbon.[2]

Some results from reduction using equal molar quantities of $LiAlH_4$ and $TiCl_4$ are provided in Table I. The yields were determined by gas chromatography using n-decane as an internal standard. The molar ratio of unsaturated hydrocarbon to $LiAlH_4$—$TiCl_4$ was optimized to obtain the highest yield of the desired reduction product with the minimum amount of hydrogen source.

Among the alkenes subjected to reduction conditions only monosubstituted double bonds were reduced with any reasonably efficient use of the hydrogen source. Disubstituted alkenes reduced only partially even in the presence of a considerable excess of reducing agent. Only 36% of cyclooctene reduced to cyclooctane under reaction conditions involving a 5 molar excess of $LiAlH_4$—$TiCl_4$. Although methylenecyclohexane reduced somewhat faster than cyclooctene (30% conversion into methylcyclohexane using a 10% molar excess of $LiAlH_4$—$TiCl_4$) continued exploration into the reactions of additional alkenes was not pursued. The sluggishness of cyclooctene toward reduction suggested that a monosubstituted alkene would be selectively consumed in the presence of a more highly substituted alkene. A fair degree of selective reduction was realized in a competitive experiment involving equal molar quantities of 1-octene and cyclooctene with a 10% molar excess of $LiAlH_4$—$TiCl_4$. Under these conditions 95% of the 1-octene was converted into n-octane, whereas only 10% of the cyclooctene was consumed.

Terminal alkynes are also reduced quite readily all the way to the alkane. Attempts to adjust conditions by limiting the amount of reducing agent in hopes of stopping at the terminal alkene stage inevitably resulted in isolation of a mixture of alkene and alkane. The rate of reaction of a monosubstituted alkene is apparently competitive with that of a terminal alkyne.

An internal alkyne is completely reduced with an equal molar amount of $LiAlH_4$—$TiCl_4$ mainly to the alkene stage. As shown in Table I, the stereochemistry of the 4-octene product depends markedly on temperature. At -40°C the percentage *trans*-4-octene produced was considerably less than at 0°C. This difference was matched almost exactly by a corresponding increase in the

Table I

Yields of Reduction Products[a]

Alkene or Alkyne	Moles of Alkene or Alkyne Used	Moles of $LiAlH_4$–$TiCl_4$ Used	Temp °C	Major Product	Yield %
1-octene	0.045	0.068	0	n-octane[b]	92
1-octyne	0.045	0.11	0	n-octane[c]	81
4-octyne	0.045	0.045	0	*cis*-4-octene *trans*-4-octene n-octane	59 <23[d] 13
4-octyne	0.045	0.045	-40	*cis*-4-octene *trans*-4-octene n-octane	73 < 7[d] 11

[a] All reactions were performed under nitrogen. Work-up involved addition of 20% aqueous ammonium chloride solution. [b] A small amount (2.3%) of 1-octene remained unreduced. [c] A small amount (3.0%) of 1-octene was also present. [d] The two isomeric 4-octenes were not completely resolved on the gas chromatogram.

percentage *cis* isomer formed at the lower temperature. However, continued lowering of temperature (-78°C) appeared not to affect the *cis/trans* ratio further. The reaction represents a reasonably stereoselective synthesis of a *cis* double bond from an appropriate internal alkyne.

Acknowledgments

Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation under Grant GP-44054X for support of this research.

References

1. a) H. A. Martin, M. van Gorkom and R. O. DeJongh, *J. Organometal. Chem.*, 36, 93 (1972). b) P. C. Wailes, H. Weigold and A. P. Bell, *ibid.*, 43, C32, (1972). c) C. Moise, J-C LeBlanc and J. Tirouflet, *Tetrahedron Letters*, 4549 (1973). d) E. Colomer and R. Corriu, *J. Organometal. Chem.*, 82, 367 (1974). e) D. W. Hart and J. Schwartz, *J. Amer. Chem. Soc.*, 96, 8115 (1975). f) D. W. Hart, T. F. Blackburn and J. Schwartz, *ibid.*, 97, 679 (1974).
2. Initial results indicate that reduction can also be accomplished by adding an ethereal solution of $LiAlH_4$ to an ethereal solution of $(Cp)_2TiCl_2$ containing the unsaturated hydrocarbon.