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REDUCTION OF ORGANIC COMPOUNDS WITH LOW-VALENT NIOBIUM ($NbCl_5/NaAlH_4$)[1)]

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Carbonyl compounds have been deoxygenatively dimerized to alkenes with the title reagent. Deoxygenation of epoxides to alkenes, reductive coupling of allylic and benzylic alcohols to hydrocarbons, and reduction of alkynes to alkenes are also described.

Recent interest has been focused on low-valent transition metals as reducing agents in organic synthesis.[2)] Here we wish to report that a niobium reagent prepared by treating $NbCl_5$ with $NaAlH_4$ is capable of carrying out reductions of several types of organic systems.

Table 1 lists the results of the reduction of aldehydes and ketones producing dimeric olefins. Aromatic carbonyl compounds reacted smoothly, but purely aliphatic ones only sluggishly. Among many reductants, $NaAlH_4$ gave the best results[3)] and the optimum ratio of $NbCl_5/NaAlH_4$/carbonyl compound was 2:1:1.[4)] A typical experimental procedure is as follows: A solution of $NaAlH_4$[5)] in THF (1.0*M*, 1.0 ml, 1.0 mmol) was added to a solution of $NbCl_5$ (0.54 g, 2.0 mmol) in benzene-THF[6)] (40:1, 10 ml) at 0°C under argon atmosphere. Instantaneous reaction occurred under an evolution of gas to give a black suspension. After 10 min, a solution of *p*-chlorobenzaldehyde (0.14 g, 1.0 mmol) in benzene (3 ml) was added dropwise and the resulting mixture was heated at reflux for 3 h. The mixture was diluted with ether (20 ml) and treated with 15% NaOH solution (0.5 ml) and anhydrous $MgSO_4$ (5 g). The semi-solid mixture was filtered through a pad of Celite 545 and the remaining solid was repeatedly washed with ether. The combined filtrate and washings were washed with 1*N* HCl and brine. Purification by silica gel column chromatography (hexane) afforded *p*,*p*'-dichlorostilbene (0.12 g, *E*/*Z* = >20:1) in 95% yield.

Both allylic and benzylic alcohols dimerized with loss of the hydroxyl group in good yields (Table 2). On treatment of 4-methyl-3-penten-2-ol with $NbCl_5/NaAlH_4$, coupling occurred with allylic rearrangement leading to mixtures. Allylic bromides, 3-bromocyclohexene and 3-bromocyclooctene, have been transformed similarly to the corresponding hydrocarbons in 82% and 71% yields,

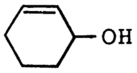
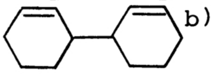
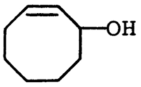
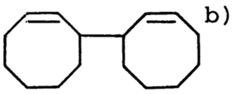
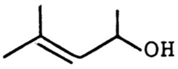
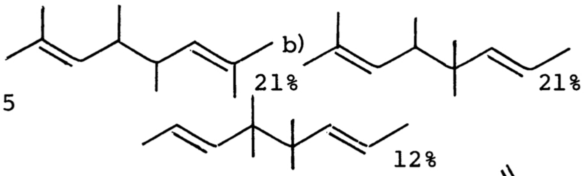
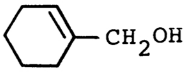
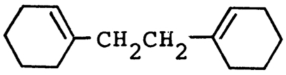
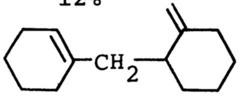
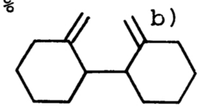
Table 1. Direct Deoxygenation of Aldehydes and Ketones to Alkenes with $NbCl_5/NaAlH_4$[a)]

Carbonyl Compound	Reaction Time (h)	Product	Yield[b)] (%)	*E/Z*
Benzaldehyde	1	Stilbene	70	>20/1[c)]
p-Chlorobenzaldehyde	3	*p,p'*-Dichlorostilbene	95	>20/1
p-Methoxybenzaldehyde	3	*p,p'*-Dimethoxystilbene	56	>20/1
Acetophenone	2	2,3-Diphenyl-2-butene	73	1/9[d)]
Benzophenone	2	Tetraphenylethylene	75	——
2-Heptanone	3	6,7-Dimethyl-6-dodecene	33	——
Decanal	5	10-Eicosene	trace	——

a) One mol of carbonyl compound, two mol of $NbCl_5$, and one mol of $NaAlH_4$ were employed. Reactions were performed at 80°C. b) Yields represent isolated purified products. c) See ref. 7. d) See ref. 8.

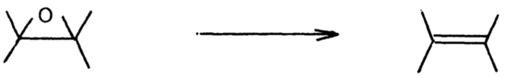
Table 2. Reductive Coupling of Alcohols Using $NbCl_5/NaAlH_4$[a)]

$$2ROH + NbCl_5/NaAlH_4 \longrightarrow R\text{-}R$$

Alcohol	Reaction Conditions		Isolated Yield(%) of R-R	
	Temp(°C)	Time(h)		
$PhCH(OH)CH_3$	80	0.5	$PhCH(CH_3)CH(CH_3)Ph$[b)]	80
Ph_2CHOH	80	0.5	$Ph_2CHCHPh_2$	90
	80	2		75
	80	2		68
	25,2;	80,0.5		
	80	2	 I 29%  II 23%  III 8%	

a) One mol of alcohol, 1.2 mol of $NbCl_5$, and 1.2 mol of $NaAlH_4$ were employed.
b) Ratio of *dl*:*meso* = 1:1.

Table 3. Deoxygenation of Epoxides with $NbCl_5/NaAlH_4$[a)]



Reactant	Reaction Conditions Temp(°C)	Time(h)	Product	Yield[b)] (%)	*E/Z*
E-Cyclododecene oxide	80	1	Cyclododecene	53	87/13
Z-Cyclododecene oxide	80	1	Cyclododecene	50	71/29
E-Stilbene oxide	25	1	Stilbene	75	*E* only
1-Dodecene oxide	80	15	1-Dodecene	50	——

a) A molar ratio of 2:1:1 $NbCl_5/NaAlH_4$/epoxide was used. b) Yields were determined by GLC using an internal standard.

Table 4. Reduction of Alkynes with $NbCl_5/NaAlH_4$[a)]

Alkyne	Reaction Conditions Temp(°C)	Time(h)	Product	Yield[b)] (%)	*E/Z*
6-Dodecyne	25	2	6-Dodecene	62	<1/20
Cyclododecyne	25	2	Cyclododecene	53	<1/20
PhC≡CPh	80	4	PhCH=CHPh	57	1/15
$PhC{\equiv}C(CH_2)_4CH_3$	80	1	$PhCH{=}CH(CH_2)_4CH_3$	60	<1/20

a) A molar ratio of 1.5:1.5:1.0 $NbCl_5/NaAlH_4$/alkyne was used. b) Yields were determined by GLC using an internal standard. The products were contaminated by <2% saturated hydrocarbons.

respectively.[9)] The lack of stereospecificity observed in the *Z*- and *E*-cyclododecene oxides (Table 3) may suggest stepwise deoxygenation through a radical intermediate.

The reagent has also been found to be effective for the reduction of alkynes. High stereoselectivity was observed in the reduction of internal alkynes to the corresponding *Z* alkenes. The $NbCl_5/NaAlH_4$ shows higher preference of *Z* products than $TiCl_4/LiAlH_4$.[10)] Attempt to reduce alkynes catalytically by Cp_2NbCl_2-$NaAlH_4$ system failed.[11,12)]

References

1) Dedicated to Professor Hitosi Nozaki on the occasion of his 60th birthday.
2) For a recent review, see T-L. Ho, *Synthesis*, 1979, 1. Ti: (a) T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, 1973, 1041. (b) J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *J. Org. Chem.*,

43, 3255 (1978); J. E. McMurry, M. G. Silvestri, M. P. Fleming, T. Hoz, and M. W. Grayston, *ibid.*, 43, 3249 (1978). (c) E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, *ibid.*, 41, 260 (1976). Cr: (a) J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, 24, 3503 (1968). (b) Y. Okude, S. Hirano, T. Hiyama, and H. Nozaki, *J. Am. Chem. Soc.*, 99, 3179 (1977); T. Hiyama, K. Kimura, and H. Nozaki, *Tetrahedron Lett.*, 22, 1037 (1980). W: (a) K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood, *J. Am. Chem. Soc.*, 94, 6538 (1972). (b) Y. Fujiwara, R. Ishikawa, F. Akiyama, and S. Teranishi, *J. Org. Chem.*, 43, 2477 (1978). Zr: F. Sato, S. Sato, and M. Sato, *J. Organomet. Chem.*, 122, C25 (1976). Fe: (a) H. Alper and D. D. Roches, *Tetrahedron Lett.*, 1977, 4155. (b) T. Fujisawa, K. Sugimoto, and H. Ohta, *Chem. Lett.*, 1974, 883. Sm and Yb: H. B. Kagan, J. L. Namy, and P. Girard, *Tetrahedron Supplement*, 37, 175 (1981).

3) In an attempt to find the suitable reducing agent, we studied the coupling reaction of benzaldehyde with a variety of combinations. The yields of stilbene were 70% ($NbCl_5/NaAlH_4$(2:1)), 32% ($NbCl_5/LiAlH_4$(2:1.5)), 15% ($NbCl_5$/n-BuLi(2:6)), and 0% ($NbCl_5$/Zn and $NbCl_5$/Mg).

4) The reaction of benzaldehyde was examined with a variety of reagents derived from different molar ratios between $NbCl_5$ and $NaAlH_4$. The yields of stilbene were 70% (2:1), 59% (2:1.5), 22% (2:2), and 25% (2:0.5).

5) We thank Nippon Aluminum Alkyls, Ltd. for gift of $NaAlH_4$.

6) Addition of THF (2 ml) to a suspension of $NbCl_5$ (4.43 g, 16.4 mmol) in benzene (80 ml) gave a homogeneous orange solution. The use of the solution is recommended because of reproducible results.

7) Both *Z*- and *E*-stilbene were found to be stable to the reaction conditions.

8) The stereochemical identities were established by hydrogenating the products (H_2 1 atm, Pd-C, EtOH) to *dl*- or *meso*-2,3-diphenylbutane, each of which was compared spectrometrically with the corresponding authentic samples. A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, 84, 743 (1962); J. R. C. Light and H. H. Zeiss, *J. Organomet. Chem.*, 21, 517 (1970).

9) Reductive coupling of 1-bromomethylcyclohexene provided the isomeric mixture (I:II:III = 52:36:12) in 85% yield.

10) P. W. Chum and S. E. Wilson, *Tetrahedron Lett.*, 1976, 15.

11) Cp_2NbH_3 derived from Cp_2NbCl_2 and hydroaluminate reducing agent has been reported to react with dialkylacetylene affording the complex $Cp_2NbH(RC{\equiv}CR')$. J. A. Labinger and J. Schwarz, *J. Am. Chem. Soc.*, 97, 1596 (1975).

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