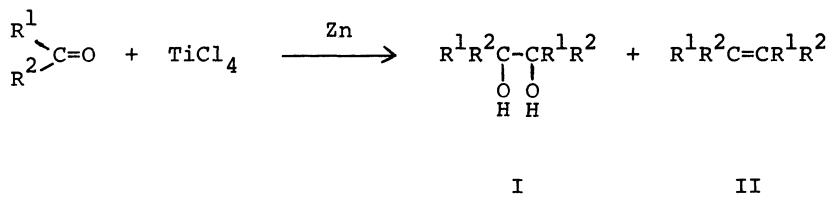


REDUCTIVE COUPLING OF CARBONYL COMPOUNDS TO PINACOLS AND OLEFINS
BY USING $TiCl_4$ AND Zn

Teruaki MUKAIYAMA, Toshio SATO, and Junichi HANNA
Laboratory of Organic Chemistry, Tokyo Institute of Technology
Okayama, Meguro-ku, Tokyo 152

Aldehydes and ketones were reduced by low valent titanium compound, produced from $TiCl_4$ and Zn, to give the corresponding pinacols and olefins in high yields.

Recently it was reported that sulfoxides,¹⁾ nitroalkanes,²⁾ and oximes³⁾ are deoxygenated by $TiCl_3$. However, the deoxygenation reaction of carbonyl compounds by utilizing low valent transition metals was only investigated by Sharpless et al.⁴⁾ We have discovered that low valent titanium compound, produced from $TiCl_4$ and Zn, reduces aldehydes and ketones to afford the corresponding pinacols (I) or olefins (II) in high yields, respectively, depending on the reaction conditions.



In a typical experiment, the suspension of zinc powder (0.59 g, 9 mmol) in 10 ml of THF was added slowly into a mixture of benzaldehyde (0.318 g, 3 mmol) and $TiCl_4$ (0.86 g, 4.5 mmol) in 20 ml of THF at $-10^\circ C$ under argon. The yellow solution immediately changed to purple and then turned dark brown. After the reaction mixture was stirred for 2 hr at $0^\circ C$, followed by alkaline hydrolysis with 10%

potassium carbonate solution and ether extraction, 1,2-diphenylethane-1,2-diol and stilbene were isolated in 98% and <1% yields, respectively. On the other hand, the deoxygenation reaction to olefins took place at an elevated temperature, for example, stilbene was obtained in 98% yield after refluxing the reaction mixture in dioxane instead of THF for 4 hr.

In a similar manner, aldehydes and ketones such as benzophenone, acetophenone, benzaldehyde, 3-phenylpropanal, and 4-phenyl-2-butanone were reduced to give the corresponding pinacols or olefins in high yields as shown in Table I. It is noteworthy that saturated aldehyde and ketone, 3-phenylpropanal and 4-phenyl-2-butanone, were reduced to the corresponding pinacols in good yields without accompanying pinacol rearrangement.

Table I. The Reactions of Carbonyl Compounds with $TiCl_4$ and Zn

Carbonyl Compounds		Reaction Conditions			Yield (%)	
R ¹	R ²	Solv.	Temp.	Time (hr)	I	II
C ₆ H ₅	C ₆ H ₅	THF	refl.	5	0	97
C ₆ H ₅	CH ₃	THF	r.t.	2	91	1
C ₆ H ₅	CH ₃	[O]	refl.	4	0	92 ^{a)}
C ₆ H ₅	H	THF	0°C	2	98	1
C ₆ H ₅	H	[O]	refl.	4	0	98 ^{b)}
C ₆ H ₅ CH ₂ CH ₂	H	[O]	85°C	6	78	0
C ₆ H ₅ CH ₂ CH ₂	CH ₃	THF	refl.	15	86	3 ^{c)}

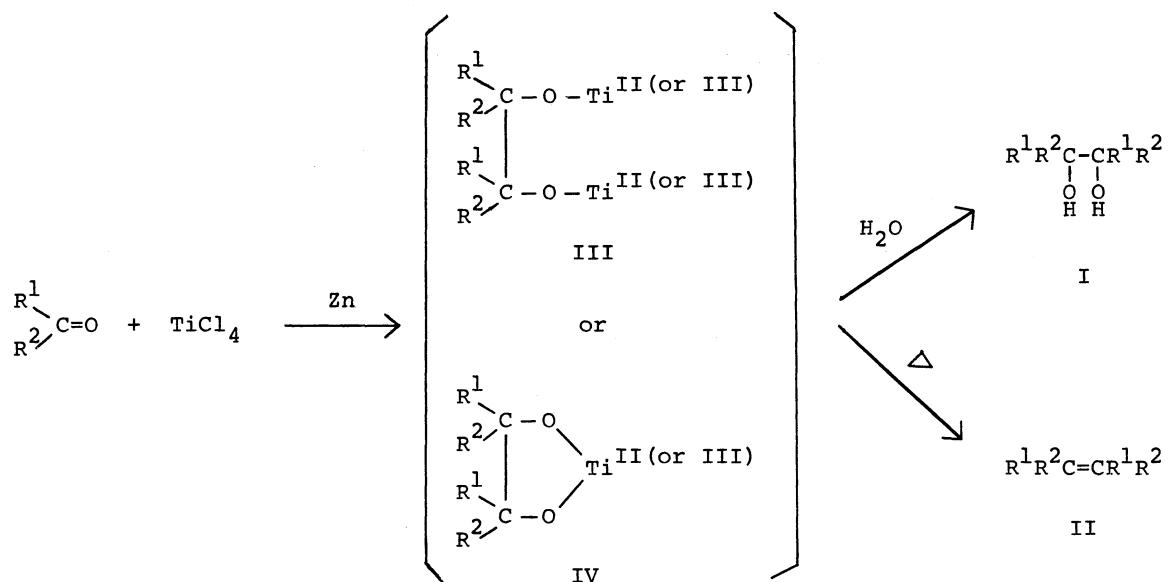
a) The ratio of cis- and trans-dimethylstilbene was 82:18.

b) Composed of more than 99% of trans-stilbene.

c) In this case, two molar amounts of $TiCl_4$ and four molar amounts of Zn to one molar amount of ketone were used.

Following points should be noted. (1) The combination of $TiCl_4$ and Zn is essential for this type of reduction. When magnesium or butyllithium was used instead of Zn in the reduction of benzophenone, tetraphenylethylene was produced in much lower yield.⁵⁾ (2) $TiCl_3$ does not reduce benzophenone in boiling THF or benzaldehyde at room temperature.⁶⁾ (3) The mole ratio of $TiCl_4$ and carbonyl compounds in their molecular complexes may probably be 1:1 or 1:2.⁷⁾ Further, by utilizing one half molar amount of $TiCl_4$ to one molar amount of carbonyl compounds, pinacol or olefin was obtained in 70-80% yield, respectively.⁸⁾ (4) In the case of benzaldehyde, the yields of 1,2-diphenylethane-1,2-diol and stilbene were 98% and <1%, respectively at 0°C in THF. Instead, the yield of the two products became 15% and 77%, respectively, when the same reaction was carried out in boiling THF for 4 hr.

Based on these facts, the reaction may be explained as follows: carbonyl compounds are reduced by $TiCl_4$ and Zn to result in an initial formation of vicinal dialkoxides (III or IV), and, in this stage, pinacols I are isolated after hydrolysis. By application of heat, the deoxygenation reaction⁹⁾ proceeds to afford olefins II.



In conclusion, it is noted that aldehydes and ketones are reduced by making use of $TiCl_4$ and Zn to give the corresponding pinacols without accompanying pinacol rearrangement or olefins in high yields.

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- 4) K. B. Sharpless, M. A. Umbreit, M. T. Nieth, and T. C. Folld, *J. Amer. Chem. Soc.*, 94, 6538 (1972).
- 5) Tetraphenylethylene was obtained only in 8% or 33% yield by making use of the combination of one molar amount of $TiCl_4$ and two molar amounts of butyl-lithium or one molar amount of $TiCl_4$ and two molar amounts of magnesium to the ketone.
- 6) Benzaldehyde was reduced by refluxing in THF for 4 hr with $TiCl_3$ to give 1,2-diphenylethane-1,2-diol in 80% yield, but no stilbene was obtained. Similarly, no tetraphenylethylene was detected by tlc when one molar amount of $TiCl_4$ and one half molar amount of Zn to benzophenone were used.
- 7) D. C. Bradley, D. C. Hancock, and W. Wardlaw, *J. Chem. Soc.*, 1952, 2773.
- 8) For example, benzaldehyde was reduced to the corresponding pinacol in 78% yield, and benzophenone was also reduced to afford tetraphenylethylene in 70% yield.
- 9) Reductive coupling of allyl alcohols via titanium dialkoxide is reported by van Tamelen and his co-workers. K. B. Sharpless, R. P. Hanzlik, and E. E. van Tamelen, *J. Amer. Chem. Soc.*, 90, 209 (1968).

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