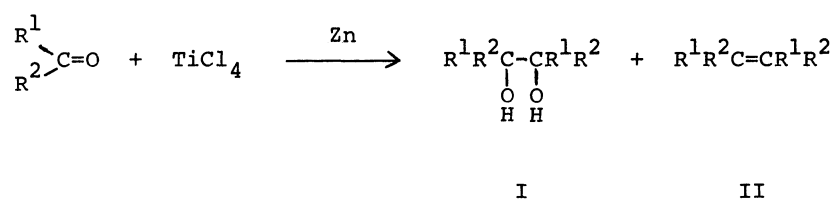


REDUCTIVE COUPLING OF CARBONYL COMPOUNDS TO PINACOLS AND OLEFINS
BY USING TiCl_4 AND Zn

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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°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°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_6H_5 | C_6H_5 | THF | refl. | 5 | 0 | 97 |
| C_6H_5 | CH_3 | THF | r.t. | 2 | 91 | 1 |
| C_6H_5 | CH_3 | $\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ | refl. | 4 | 0 | 92 ^{a)} |
| C_6H_5 | H | THF | 0°C | 2 | 98 | 1 |
| C_6H_5 | H | $\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ | refl. | 4 | 0 | 98 ^{b)} |
| $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$ | H | $\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ | 85°C | 6 | 78 | 0 |
| $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$ | CH_3 | THF | refl. | 15 | 86 | 3 ^{c)} |

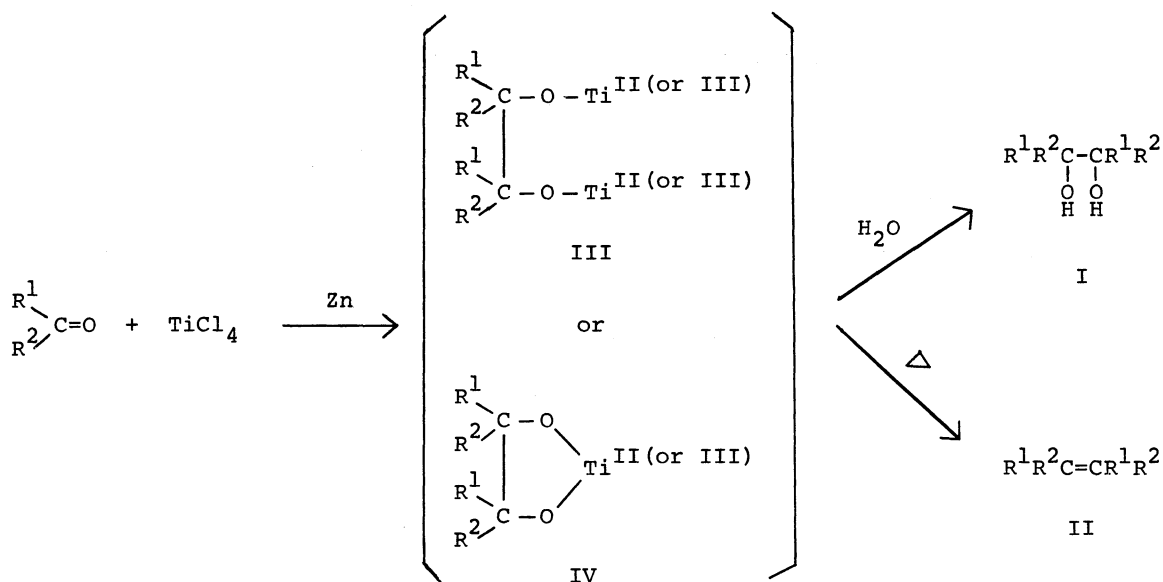
a) The ratio of cis- and trans-dimethylstilbene was 82:18.

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.

REFERENCES

- 1) T.-L. Ho and C. M. Wong, *Synthetic Communications*, 3, 37 (1973).
- 2) J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, 93, 5309 (1971).
- 3) G. H. Timms and E. Wildsmith, *Tetrahedron Lett.*, 1971, 195.
- 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 butyllithium 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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