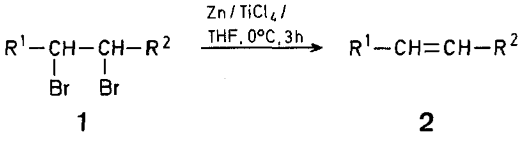
Debromination of *vic*-Dibromides with Zinc and a Catalytic Amount of Titanium(IV) Chloride in Tetrahydrofuran

Fumie SATO*, Toshio AKIYAMA, Katsumi IIDA, Masao SATO

Department of Chemical Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

Debrominations of *vic*-dibromides to alkenes using a variety of reagents have been reported[1]. Zinc dust is so far the most widely employed reagent for these purposes[2]. The reaction is usually carried out in acetic acid or ethanol. Debromination in an aprotic solvent, however, is of great interest because potential problems of substrate solubility can be eliminated. We have now found that *vic*-dibromides **1** are converted to the corresponding alkenes **2** in nearly quantitative yields and under very mild conditions by treatment with zinc dust and a catalytic amount of titanium(IV) chloride in tetrahydrofuran at 0 °C.



$$R^1-\underset{Br}{CH}-\underset{Br}{CH}-R^2 \xrightarrow[THF,\,0°C,\,3h]{Zn/TiCl_4/} R^1-CH=CH-R^2$$

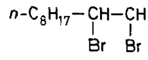
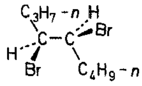
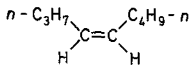
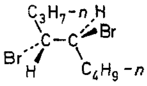
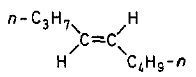
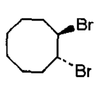
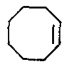
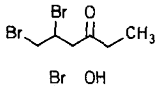
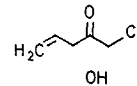
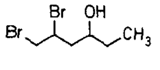
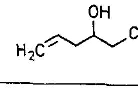
Results and the effects of variations in some reaction parameters (using 1,2-dibromodecane as the substrate) are displayed in the Table. It can be seen from the Table that, in addition to titanium(IV) chloride, other transition metal halides such as cobalt(II) chloride, chromium(III) chloride and nickel(II) chloride can be used as catalyst, but titanium(IV) chloride is the most effective. The success of this reaction is dependent on the solvent used. No reaction took place in solvents such as ether or benzene. Noteworthy here is the fact that the elimination is virtually stereoselective (Entry 8 and 9 in the Table).

Low-valent titanium compounds obtained by reduction of titanium(III) or titanium(IV) chloride with lithium aluminium hydride have been employed for dehalogenation of *vic*-dihaloalkanes[4]. This reaction, however, is not catalytic but requires a stoichiometric amount of the titanium compound. Although there are many methods available to debrominate *vic*-dibromoalkanes, we consider the method reported here to be one of the most efficient and operationally simple procedures.

Debromination of *vic*-Dibromoalkanes (1) to Alkenes (2); General Procedure:

A catalytic amount of titanium(IV) chloride (0.16 ml, 1.5 mmol) is added to a mixture of zinc dust (3.7 g, 57 mmol) and *vic*-dibromoalkane **2** (19 mmol) in tetrahydrofuran (50 ml) contained in a 100 ml Schlenk

Table. Debromination of *vic*-Dibromoalkanes **1** to Alkenes **2**

Entry	Dibromide **1**	Alkene[a] **2**	Reaction Conditions[b] Catalyst/Solvent	Yield[c] [%]	b.p. [°C]/torr found	b.p. [°C]/torr Ref.[3]
1	 $n\text{-}C_8H_{17}-\underset{Br}{CH}-\underset{Br}{CH_2}$	$n\text{-}C_8H_{17}-CH=CH_2$	none/THF	trace		
2			$TiCl_4$/THF	86 (99)	170-173°/760	170.6°/760
3			$TiCl_4$/ether	trace		
4			$TiCl_4$/benzene	trace		
5			$CoCl_2$/THF	(23)		
6			$CrCl_3$/THF	(72)		
7			$NiCl_2$/THF	(14)		
8		 (*cis/trans* = 96/4)	$TiCl_4$/THF	89 (96)	143-144°/760	144-146°/760
9		 (*cis/trans* = 1/99)	$TiCl_4$/THF	91 (98)	143-144°/760	
10			$TiCl_4$/THF	91 (100)	135-137°/760	34°/12
11			$TiCl_4$/THF	85	123-125°/760	124-124.2°/760
12			$TiCl_4$/THF	82	127-130°/760	129-131°/760

---

[a] All products were identified by comparison of their physical properties with those of authentic samples.

[b] Reaction at 0 °C for 3 h.

[c] Yield of pure product isolated by distillation; purity: >99% by G.L.C. (PEG 20 M, 5 m). Value in brackets is yield determined by G.L.C.

0039-7881/82/1232-1025 $ 03.00

flask under argon at 0 °C. The reaction mixture is then stirred for 3 h at 0 °C, and worked up by the addition of water (20 ml) and extraction with ether (3 x 20 ml). The ether extract is dried with magnesium sulfate, the solvent distilled off, and the product is isolated by distillation.

Received: June 6, 1982

---

[1] K. Fukunaga, H. Yamaguchi, *Synthesis* **1981**, 879; and references cited therein.
M. Schlosser, in Houben-Weyl, *Methoden der organischen Chemie,* 4th Edn., Vol. 5/1b, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1972, p. 180-204.

[2] S. R. Sandler, W. Karo, *Organofunctional Group Preparations,* Vol. 1, Academic Press, New York, 1968, p. 46.
J. W. McCutcheon, *Org. Synth. Coll. Vol.* III, 526 (1955).

[3] I. Heilbron, H. M. Bunbury, *Dictionary of Organic Compounds,* Eyre & Spottiswoode, London, 1965.

[4] G. A. Olah, G. K. S. Prahash, *Synthesis* **1976**, 607.

0039-7881/82/1232-1026 $ 03.00