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Communications

Reductive Debromination of *vic*-Dibromides to Alkenes with Bis(cyclopentadienyl)titanium(IV) Dichloride-Indium System

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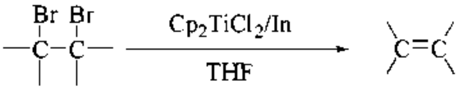
The debromination of *vic*-dibromides to alkenes is important in organic synthesis as a double bond protection-deprotection strategy.[1] A number of methods for effecting debromination have been developed, but most require long reaction times or elevated temperatures.[2] It has been reported that Cp_2TiCl_2/Zn system can be used for a reductive debromination of *vic*-dibromides **1** to alkenes **2**.[3] We have found that various *vic*-dibromides **1** on treatment with Cp_2TiCl_2/In system in THF are also smoothly converted into the corresponding alkenes **2** in good to excellent yields. In comparison with Cp_2TiCl_2/Zn system, the reactions using Cp_2TiCl_2/In system are fast and high-yielding. The chemical reactivity of Cp_2TiCl_2/M system (M=Na, Zn, Al, Mg, Sm) has been the subject of considerable interest and the reducing ability of these systems has been extensively studied.[4] Because of the close resemblance of indium to magnesium and zinc in several respects, including first ionization potential,[5] we considered that Cp_2TiCl_2/In system could also be a useful addition to the conventional methods. We report here a rapid and convenient reductive procedure for debromination of *vic*-dibromides **1** to alkenes **2** with Cp_2TiCl_2/In system under the mild conditions. The reactions can be generalized as in eq. 1.[6] The reaction molar ratio of indium and Cp_2TiCl_2 is 1 : 2. If the molar ratio is changed to In : Cp_2TiCl_2=1 : 1, the reaction is not successful. It is evident from the table that the reductive eliminations are chemoselective as aldehyde, keto, methoxy and ester groups remained unaffected under the reaction conditions. In order to assess the generality of the process, the reaction was studied with a variety of *vic*-dibromides and only *trans* olefins were obtained. The results are summarized in Table 1.



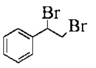
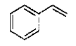
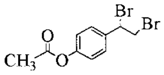
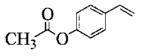
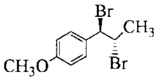
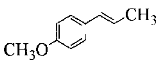
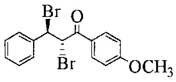
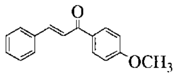
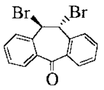
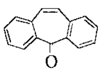
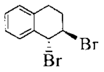
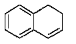
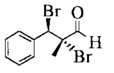
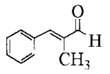
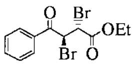
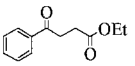
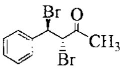
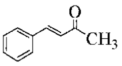
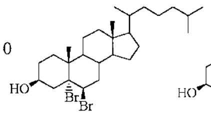
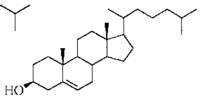
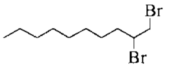
$$\text{BrC(-)(-)–C(Br)(-)} \xrightarrow[\text{THF}]{Cp_2TiCl_2/In} >C=C< \qquad (1)$$

1 **2**

All the compounds obtained showed IR, NMR and mass spectral data compatible with the structure. Although the role of bis(cyclopentadienyl)titanium(IV) dichloride is still not clarified, it is likely that reduction of titanium(IV) with indium provides low valent titanium, which reacts with *vic*-dibromides **1** to give the corresponding alkenes **2**.[7] The notable advantages of this methodology are mild reaction condition, fast reaction time (10 min), simple operation, tolerance of other functional groups. The reaction of 2,3-dibromoketoester with this reagent gave saturated ketoester as an overreduction product (entry 8). The formation of the reduced products can be conceived to proceed via alkenes by debromination of the dibromides and subsequent reduction as Khurana has suggested in his work.[8] In the case of aliphatic *vic*-dibromide, cholesterol dibromide underwent smooth debromination (entry 10), but 1,2-dibromodecane was inert (entry 11). It is assumed that the radical or anion intermediate of aliphatic *vic*-dibromide is less stable than that of the aromatic compound.

In conclusion, we have demonstrated that the dehalogenation of *vic*-dibromides with Cp_2TiCl_2/In system provided

Table 1. Reductive debromination of *vic*-dibromides with Cp_2TiCl_2/In system

Entry	Substrate	Product	Reaction time (min)	Yield (%)*
1			10	99
2			10	90
3			10	81
4			10	85
5			10	71
6			10	88
7			10	85
8			10	85
9			10	85
10			10	85
11		—	10	0

*Isolated yields.

various alkenes in good to excellent yields under the mild conditions. The reaction is rapid and the procedure is simple. Although the scope and limitations were not fully established, the present method could be a practical alternative to the conventional method. Further investigations of more useful applications are in progress.

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5. Typical Procedure: **4-Acetoxy styrene**. Bis(cyclopentadienyl)titanium(IV) dichloride (500 mg, 2.0 mmol), indium powder (115 mg, 1.0 mmol) and THF (5 mL) were mixed under nitrogen atmosphere and the resulting mixture was sirred at reflux for 30 min. A dark-red solution of the low-valent titanium-indium complex was obtained and cooled to room temperature. To this solution, 4-(1,2-dibromoethyl)phenyl acetate (entry 2, 161 mg, 0.5 mmol) was added. The reaction mixture was stirred for 10 min at room temperature under nitrogen. The solvent was evaporated under reduced pressure and the residue was diluted with ether and filtered. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 6:1) to afford the desired alkene as a colorless oil (73 mg, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz, $CDCl_3$) δ 7.44 (d, 2H, J = 6.6 Hz), 7.07 (d, 2H, J = 6.6 Hz), 6.72 (dd, 1H, J = 17.4, 11.1 Hz), 5.73 (d, 1H, J = 17.4 Hz), 5.27 (d, 1H, J = 11.1 Hz), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) 169.9, 150.6, 136.3, 135.8, 127.6, 122.1, 114.5, 21.6. GC-MS m/z: 162 (M^+). IR (film, cm^{-1}) 3076, 1770, 1641, 1601, 1516, 1372, 1212, 1023.
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