

## Organotitanium chemistry

### XVIII \*. Dehalogenation of organic halides by $\text{Cp}_2\text{TiX}$ (X = Cl, Br)

**Qian Yanlong \*\*, Li Guisheng, and Yao-Zeng Huang**

*Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai (China)*

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#### Abstract

Dicyclopentadienyltitanium chloride and bromide prepared in situ from the reduction of dicyclopentadienyltitanium dichloride by isopropylmagnesium chloride and bromide, respectively, are effective dehalogenating reagents for benzylic, allylic halides and  $\alpha$ -bromoketones. Benzylic and allylic halides are transformed into the coupling products whereas the  $\alpha$ -bromoketones are reduced to the corresponding ketones in satisfactory yields under mild conditions.

#### Introduction

Dicyclopentadienyltitanium chloride has been prepared either by the reduction of dicyclopentadienyltitanium dichloride by zinc [1], aluminium [2] or by the reactions of titanium trichloride with cyclopentadienides [3,4]. Its dimeric chloro-bridged structure has been well characterized by X-ray diffraction methods [5]. Dicyclopentadienyltitanium chloride easily undergoes oxidative addition reactions with alkyl disulfides, azides [6],  $\text{CCl}_4$  [7] and coordination reactions with nitrogen- and phosphorus-containing ligands [1,8] as well as deoxygenation of some inorganic [9,10] and organic substrates [11]. Several other low-valent titanium reagents have been employed in dehalogenation of organic halides. Alkyl, vinyl and aryl halides can be reduced by  $\text{Cp}_2\text{TiCl}_2/\text{Mg}$  [12],  $\text{TiCl}_3/\text{LiAlH}_4$  [13] and  $\text{TiCl}_4/\text{LiAlH}_4$  [14], while benzylic and allylic halides can be coupled by  $\text{TiCl}_4/\text{LiAlH}_4$  [15] and "titanocene" [16], but the latter gives rather poor yield. We find dicyclopentadienyltitanium halides in situ from the reduction of  $\text{Cp}_2\text{TiCl}_2$  by isopropylmag-

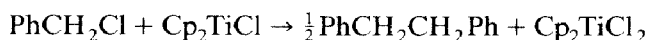
\* For part XVII see ref. 23.

\*\* Author to whom correspondence should be addressed.

nesium halides are very effective towards the dehalogenation of benzylic, allylic halides and  $\alpha$ -bromoketone. It is easy to carry out the process under mild reaction conditions and the starting material,  $\text{Cp}_2\text{TiCl}_2$ , can be recovered.

## Results and discussion

When benzyl chloride is added to the THF solution of  $\text{Cp}_2\text{TiCl}$  from the reduction of  $\text{Cp}_2\text{TiCl}_2$  by Al [2], the reaction mixture becomes red immediately and red solid precipitates. After work-up, dibenzyl is obtained in 86% yield and the red solid is shown to be  $\text{Cp}_2\text{TiCl}_2$ . In this reaction, the C–Cl bond in benzyl chloride is cleaved and the chlorine atom is transferred to  $\text{Cp}_2\text{TiCl}$  to produce the stable +4 valent titanium compound  $\text{Cp}_2\text{TiCl}_2$ , accompanied by the formation of dibenzyl as shown in the following equation.



Compounds  $\text{Cp}_2\text{TiCl}$  and  $\text{Cp}_2\text{TiBr}$  generated in situ from the reactions of  $\text{Cp}_2\text{TiCl}_2$  with  $i\text{-C}_3\text{H}_7\text{MgCl}$  and  $i\text{-C}_3\text{H}_7\text{MgBr}$  respectively in 1/1 molar ratio [17] can also act as good dehalogenating reagents for benzylic and allylic halides. The results are listed in Table 1.

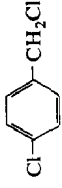
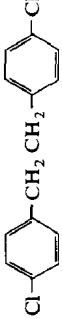
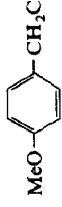
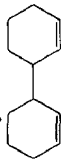
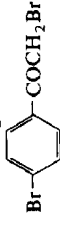
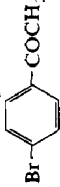
It is interesting to note that  $\text{Cp}_2\text{TiCl}_2$  is produced in the reaction of  $\text{Cp}_2\text{TiCl}$  with benzylic and allylic chlorides. For example,  $\text{Cp}_2\text{TiCl}_2$  in pure form is recovered in 82% yield from the reaction of  $\text{Cp}_2\text{TiCl}$  and  $\text{BzCl}$  ( $\text{Bz}$  = benzyl). Although  $\text{Cp}_2\text{TiCl}_2$  can be regenerated in the course of reaction, it cannot catalyze the coupling of  $\text{BzCl}$  by  $i\text{-C}_3\text{H}_7\text{MgCl}$ , in which case, the normal nucleophilic substitution between  $i\text{-C}_3\text{H}_7\text{MgCl}$  and  $\text{BzCl}$  predominates. It is, however, possible to realize the coupling reaction by using a catalytic amount of  $\text{Cp}_2\text{TiCl}_2$ , since  $\text{Cp}_2\text{TiCl}_2$  formed during the coupling reaction is reusable without isolation, that means,  $\text{Cp}_2\text{TiCl}$  in situ from  $\text{Cp}_2\text{TiCl}_2$  and  $i\text{-C}_3\text{H}_7\text{MgCl}$  reacts with equivalent  $\text{BzCl}$  and the resulting  $\text{Cp}_2\text{TiCl}_2$  is reduced by addition of another portion of  $i\text{-C}_3\text{H}_7\text{MgCl}$  to  $\text{Cp}_2\text{TiCl}$ , which again reacts with  $\text{BzCl}$  and the recyclicalization continues. Thus 81% total conversion of  $\text{BzCl}$  is obtained after three such cycles.

If one mole of allyl chloride is added to the mixture from the full reaction of two moles of  $\text{Cp}_2\text{TiCl}$  and one mole of  $\text{BzCl}$ , the cross coupling product,  $\text{PhCH}_2\text{CH}_2\text{CH}=\text{CH}_2$  is also obtained in addition to dibenzyl and diallyl (32/35/33 in mole). The ratio of the three depends greatly on the reaction conditions. Toluene is also found to be present in the products after the reaction mixture from  $\text{Cp}_2\text{TiCl}$  and  $\text{BzCl}$  (2/1) is quenched by dilute hydrochloric acid. These facts suggest that formation of the compound  $\text{Cp}_2\text{Ti}(\text{Cl})\text{CH}_2\text{Ph}$  (III) in the reaction of  $\text{Cp}_2\text{TiCl}$  with  $\text{BzCl}$  is possible.

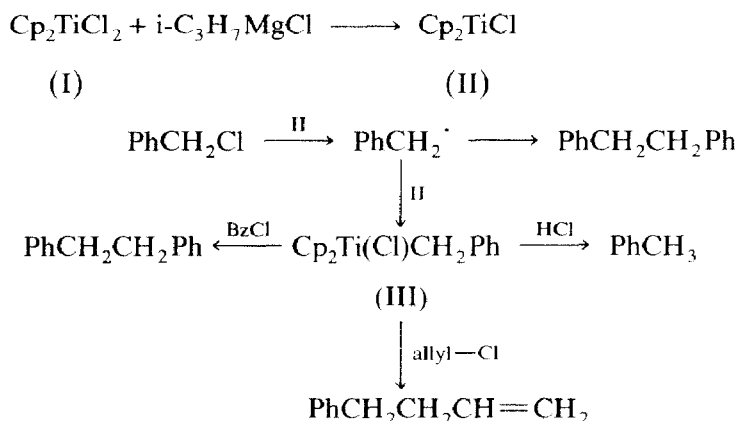
Compound III is stable at room temperature and decomposes to approximately equal amounts of dibenzyl and toluene on thermolysis [18,19]. The formation of III may arise from the combination of  $\text{Cp}_2\text{TiCl}$  and benzyl radical coming from the cleavage of benzylic C–Cl by  $\text{Cp}_2\text{TiCl}$ , which can also dimerize to give dibenzyl. Reactions of compound III with electrophiles such as allyl chloride and protons result in the corresponding products. The pathway of the reaction between  $\text{Cp}_2\text{TiCl}$  and benzylic and allylic halides is illustrated by the example of  $\text{BzCl}$  given in Scheme 1.

Table 1

Dehalogenation of benzylic, allylic halides and  $\alpha$ -bromoketones by  $\text{Cp}_2\text{TiX}$  (X = Cl, Br) <sup>a</sup>

| Entry | R-X                                                                                   | $\text{Cp}_2\text{TiX}^b$ | Product                                                                                        | Yield <sup>c</sup>          | M.p./b.p.<br>(°C) (lit.) | NMR (ppm)                                            |
|-------|---------------------------------------------------------------------------------------|---------------------------|------------------------------------------------------------------------------------------------|-----------------------------|--------------------------|------------------------------------------------------|
| 1     | BzCl                                                                                  | A                         | Bz-Bz                                                                                          | 86                          | 52-53<br>(52.2)          | 7.10(s, 5H), 2.87(s, 2H)                             |
| 2     | BzCl                                                                                  | B                         |                                                                                                | 90                          |                          |                                                      |
| 3     | BzCl                                                                                  | C                         |                                                                                                | 95                          |                          |                                                      |
| 4     | BzBr                                                                                  | C                         |                                                                                                | 95                          |                          |                                                      |
| 5     | BzI                                                                                   | C                         |                                                                                                | 88                          |                          |                                                      |
| 6     | $\text{Ph}_2\text{CHCl}$                                                              | C                         | $\text{Ph}_2\text{CHCHPh}_2$                                                                   | 76                          | 214-216<br>(214-215)     | 6.99(s, 10H), 4.60(s, 1H)                            |
| 7     | $\text{PhCHCl}$<br> <br>Et                                                            | C                         | $\text{PhCH-CHPh}$<br> <br>Et                                                                  | 59                          | 89-91(88)                | 7.19(s, 5H), 2.50(m, 1H)<br>1.33(m, 2H), 0.52(t, 3H) |
| 8     |    | C                         |              | 82                          | 98-99(102)               | 7.05(m, 4H), 2.80(s, 2H)                             |
| 9     |    | C                         |              | 90                          | 82-83                    | 6.85(m, 4H), 3.75(s, 3H)                             |
| 10    | $\text{PhCHCl}_2$                                                                     | B                         | <i>trans</i> -stilbene                                                                         | 17                          | (83-84)<br>124-125       | 2.78(s, 2H)<br>7.25(m, 5H), 6.95(s, 1H)              |
| 11    | $\text{PhCCl}_3$                                                                      | B                         | tolan                                                                                          | 78                          | (124-125)<br>68-69(64)   | 7.06-7.46(m)                                         |
| 12    | allyl-Cl                                                                              | C                         | diallyl<br> | <sup>d</sup>                |                          |                                                      |
| 13    |    | C                         |                                                                                                | 96                          |                          | 5.58(s, 2H)                                          |
| 14    | BzCl + allyl-Cl                                                                       | B                         | Bz-Bz<br>Bz-allyl<br>diallyl                                                                   | 35 <sup>d</sup><br>32<br>33 |                          | 1.50-2.30(m, 7H)                                     |
| 15    | $\text{CH}_3\text{COCH}_2\text{Br}$                                                   | B                         | $\text{CH}_3\text{COCH}_3$                                                                     | <sup>d</sup>                |                          |                                                      |
| 16    | $\text{PhCOCH}_2\text{Br}$                                                            | B                         | $\text{PhCOCH}_3$                                                                              | 92                          |                          | 7.85(m, 2H), 7.40(m, 3H)                             |
| 17    |  | B                         |           | 85                          | 51-52(50-51)             | 7.58(m, 4H), 2.40(m, 3H)                             |
| 18    | $\text{PhCOCH}_2\text{CH}_3$<br> <br>Br                                               | B                         | $\text{PhCOCH}_2\text{CH}_3$                                                                   | 75                          | 70/2<br>(92/10)          | 7.80(m, 5H), 2.31(q, 2H)<br>1.10(t, 3H)              |

<sup>a</sup> The molar ratio of  $\text{Cp}_2\text{TiX}$  to benzylic and allylic halides is 1/1 (based on one halogen atom); while that of  $\text{Cp}_2\text{TiCl}$  to  $\alpha$ -bromoketones is 2/1. <sup>b</sup> A stands for isolated  $\text{Cp}_2\text{TiCl}$  from  $\text{Cp}_2\text{TiCl}_2 + \text{Al}$ ; B and C stand for  $\text{Cp}_2\text{TiCl}$  and  $\text{Cp}_2\text{TiBr}$  in situ from  $\text{Cp}_2\text{TiCl}_2 + i\text{-C}_3\text{H}_7\text{MgCl}$  and  $\text{Cp}_2\text{TiCl}_2 + i\text{-C}_3\text{H}_7\text{MgBr}$ , respectively. <sup>c</sup> Isolated yield unless indicated. <sup>d</sup> Detected by GLC.

Scheme 1. The reaction of BzCl and  $\text{Cp}_2\text{TiCl}$ .

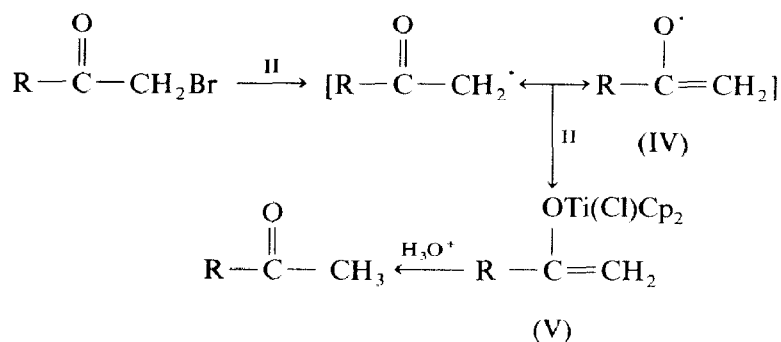
Reactions of  $\text{Cp}_2\text{TiCl}$  with benzal chloride and benzo-trichloride in the molar ratios of 2/1 and 3/1 produce *trans*-stilbene and tolan respectively.

$\alpha$ -Bromoketones are also reactive towards dicyclopentadienyltitanium chloride. They differ from benzylic and allylic halides by requiring two moles of  $\text{Cp}_2\text{TiCl}$  per mole of the  $\alpha$ -bromoketones to complete the reactions. The first mole of  $\text{Cp}_2\text{TiCl}$  possibly abstracts the bromine atom of the  $\alpha$ -bromoketone and the resulting radical IV combines with the second mole of  $\text{Cp}_2\text{TiCl}$  to form the stable titanium enolate V [20], which fails to react with the halide. The coupling reaction of IV is completely suppressed by the formation of V and hydrolysis of V by hydrochloric acid gives the reduction product, namely the corresponding ketone as outlined in Scheme 2.

Under similar conditions, alkyl and aryl halides such as  $\text{PhCH}_2\text{CH}_2\text{Cl}$ , EtBr and PhBr fail to react with  $\text{Cp}_2\text{TiCl}$ . In this connection,  $\text{Cp}_2\text{TiCl}$  differs from  $\text{Cp}_2\text{TiCl}_2/\text{Mg}$  [12] and vanadocene [21,22].

## Experimental

Ether and tetrahydrofuran were dried over  $\text{Na-Ph}_2\text{CO}$  and degassed before distillation. NMR spectra were recorded on a Varian EM-360A (60 MHz) NMR Spectrometer using  $\text{CCl}_4$  as solvent and TMS as internal standard. Melting points were measured by means of a Thiele tube and not corrected.

Scheme 2. Reduction of  $\alpha$ -bromoketones by  $\text{Cp}_2\text{TiCl}$ .

Typical procedures are as follows: Preparation of  $\text{Cp}_2\text{TiCl}$ . To  $\text{Cp}_2\text{TiCl}_2$  (1.0 g) in 5 ml of THF was added 4 ml of  $i\text{-C}_3\text{H}_7\text{MgCl}$  (1.0 *M* in  $\text{Et}_2\text{O}$ ) under argon atmosphere. The resulting mixture was stirred at room temperature for 0.5 h. The green  $\text{Cp}_2\text{TiCl}$  so-formed was used without isolation in the following reactions.

Reaction of  $\text{BzCl}$  with  $\text{Cp}_2\text{TiCl}$ . Benzyl chloride (0.46 ml, 4 mmol) was added to  $\text{Cp}_2\text{TiCl}$  (4 mmol) prepared in situ as above. The reaction mixture turned red immediately and was stirred at room temperature for 5 h. After removal of the solvents, petroleum (50 ml) was added to the residue. The solid was filtered off and extracted with chloroform. Concentration of the chloroform solution gives  $\text{Cp}_2\text{TiCl}_2$  (820 mg) in 82% yield. The filtrate was passed through a 5 cm column of silica gel and eluted with petroleum. The petroleum solution was concentrated to afford colorless needle crystals (328 mg) of dibenzyl in 90% yield.

Reaction of  $\text{BzCl}$  using catalytic amount of  $\text{Cp}_2\text{TiCl}_2$ .  $\text{BzCl}$  (0.23 ml, 2 mmol) was added to  $\text{Cp}_2\text{TiCl}$  (2 mmol). After 5 h, 2.0 ml of  $i\text{-C}_3\text{H}_7\text{MgCl}$  (2 mmol) was added to the red reaction mixture and stirred for 0.5 h. Then  $\text{BzCl}$  (2 mmol) was added and the mixture was stirred for 5 h again. After 3 such cycles, the reaction mixture was treated as above and 600 mg of colorless liquid was obtained.  $^1\text{H}$  NMR showed it was composed of 74% of dibenzyl and 26% of  $\text{BzCl}$  (in weight), corresponding to 81% total conversion of  $\text{BzCl}$ .

Cross coupling of  $\text{BzCl}$  and allyl- $\text{Cl}$ .  $\text{BzCl}$  (0.23 ml, 2 mmol) was added to  $\text{Cp}_2\text{TiCl}$ . After 10 h stirring, allyl chloride (0.17 ml, 2 mmol) was added to the dark-violet mixture and stirred for another 2 h. The red solid was filtered off and the filtrate was quantitatively analyzed by GLC compared with authentic samples. The molar ratio of dibenzyl,  $\text{PhCH}_2\text{CH}_2\text{CH}=\text{CH}_2$  and diallyl was 35/32/33.

Reaction of  $\text{PhCHCl}_2$  with  $\text{Cp}_2\text{TiCl}$ . Benzalchloride (0.25 ml, 2 mmol) was added to  $\text{Cp}_2\text{TiCl}$  (4 mmol). After the usual work-up, the crude product was recrystallized from  $\text{EtOH}/\text{H}_2\text{O}$  to give 30 mg of *trans*-stilbene in 17% yield.

Reaction of 2,4'-dibromoacetophenone with  $\text{Cp}_2\text{TiCl}$ . 2,4'-dibromoacetophenone (556 mg) in THF (5 ml) was added to  $\text{Cp}_2\text{TiCl}$  (4 mmol) and the resulting red mixture was stirred at room temperature for 5 h. Then 2*N*  $\text{HCl}$  (5 ml) and petroleum (50 ml) was added. The petroleum solution was separated from the filtrate, dried over  $\text{Na}_2\text{SO}_4$  and concentrated to give crystalline solid (340 mg) in 85% yield.

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