Journal of Organometallic Chemistry, 381 (1990) 29–34
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20416

Organotitanium chemistry

XVIII *. Dehalogenation of organic halides by Cp_2TiX ($X = Cl, Br$)

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(Received June 7th, 1989)

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 α-bromoketones. Benzylic and allylic halides are transformed into the coupling products whereas the α-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], 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 Cp_2TiCl_2/Mg [12], $TiCl_3/LiAlH_4$ [13] and $TiCl_4/LiAlH_4$ [14], while benzylic and allylic halides can be coupled by $TiCl_4/LiAlH_4$ [15] and "titanocene" [16], but the latter gives rather poor yield. We find dicyclopentadienyltitanium halides in situ from the reduction of Cp_2TiCl_2 by isopropylmag-

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* For part XVII see ref. 23.

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nesium halides are very effective towwards the dehalogenation of benzylic, allylic halides and α-bromoketone. It is easy to carry out the process under mild reaction conditions and the starting material, Cp_2TiCl_2, can be recovered.

Results and discussion

When benzyl chloride is added to the THF solution of Cp_2TiCl from the reduction of Cp_2TiCl_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 Cp_2TiCl_2. In this reaction, the C–Cl bond in benzyl chloride is cleaved and the chlorine atom is transferred to Cp_2TiCl to produce the stable +4 valent titanium compound Cp_2TiCl_2, accompanied by the formation of dibenzyl as shown in the following equation.

$$PhCH_2Cl + Cp_2TiCl \rightarrow \tfrac{1}{2}PhCH_2CH_2Ph + Cp_2TiCl_2$$

Compounds Cp_2TiCl and Cp_2TiBr generated in situ from the reactions of Cp_2TiCl_2 with i-C_3H_7MgCl and i-C_3H_7MgBr 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.

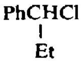
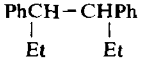
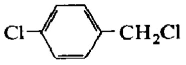
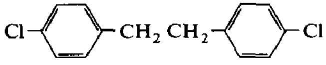
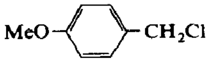
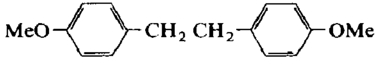
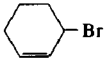
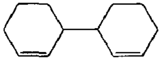
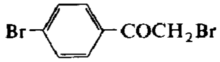
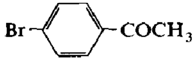
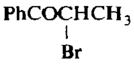
It is interesting to note that Cp_2TiCl_2 is produced in the reaction of Cp_2TiCl with benzylic and allylic chlorides. For example, Cp_2TiCl_2 in pure form is recovered in 82% yield from the reaction of Cp_2TiCl and BzCl (Bz = benzyl). Although Cp_2TiCl_2 can be regenerated in the course of reaction, it cannot catalyze the coupling of BzCl by i-C_3H_7MgCl, in which case, the normal nucleophilic substitution between i-C_3H_7MgCl and BzCl predominates. It is, however, possible to realize the coupling reaction by using a catalytic amount of Cp_2TiCl_2, since Cp_2TiCl_2 formed during the coupling reaction is reusable without isolation, that means, Cp_2TiCl in situ from Cp_2TiCl_2 and i-C_3H_7MgCl reacts with equivalent BzCl and the resulting Cp_2TiCl_2 is reduced by addition of another portion of i-C_3H_7MgCl to Cp_2TiCl, which again reacts with BzCl and the recyclization continues. Thus 81% total conversion of 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 Cp_2TiCl and one mole of BzCl, the cross coupling product, $PhCH_2CH_2CH{=}CH_2$ 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 Cp_2TiCl and BzCl (2/1) is quenched by dilute hydrochloric acid. These facts suggest that formation of the compound $Cp_2Ti(Cl)CH_2Ph$ (III) in the reaction of Cp_2TiCl with 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 Cp_2TiCl and benzyl radical coming from the cleavage of benzylic C–Cl by Cp_2TiCl, 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 Cp_2TiCl and benzylic and allylic halides is illustrated by the example of BzCl given in Scheme 1.

Table 1

Dehalogenation of benzylic, allylic halides and α-bromoketones by Cp_2TiX (X = Cl, Br) [a]

Entry	R–X	Cp_2TiX [b]	Product	Yield [c]	M.p./b.p. (°C) (lit.)	NMR (ppm)
1	BzCl	A	Bz–Bz	86	52–53	7.10(s, 5H), 2.87(s, 2H)
2	BzCl	B		90	(52.2)	
3	BzCl	C		95		
4	BzBr	C		95		
5	BzI	C		88		
6	Ph_2CHCl	C	$Ph_2CHCHPh_2$	76	214–216 (214–215)	6.99(s, 10H), 4.60(s, 1H)
7	 $\underset{\mathrm{Et}}{\mathrm{PhCHCl}}$	C	 $\underset{\mathrm{Et}}{\mathrm{PhCH}}-\underset{\mathrm{Et}}{\mathrm{CHPh}}$	59	89–91(88)	7.19(s, 5H), 2.50(m, 1H) 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 (83–84)	6.85(m, 4H), 3.75(s, 3H) 2.78(s, 2H)
10	$PhCHCl_2$	B	*trans*-stilbene	17	124–125 (124–125)	7.25(m, 5H), 6.95(s, 1H)
11	$PhCCl_3$	B	tolan	78	68–69(64)	7.06–7.46(m)
12	allyl—Cl	C	diallyl	[d]		
13		C		96		5.58(s, 2H) 1.50–2.30(m, 7H)
14	BzCl + allyl–Cl	B	Bz–Bz Bz–allyl diallyl	35 [d] 32 33		
15	CH_3COCH_2Br	B	CH_3COCH_3	[d]		
16	$PhCOCH_2Br$	B	$PhCOCH_3$	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	 $\underset{\mathrm{Br}}{\mathrm{PhCOCH}}\mathrm{CH_3}$	B	$PhCOCH_2CH_3$	75	70/2 (92/10)	7.80(m, 5H), 2.31(q, 2H) 1.10(t, 3H)

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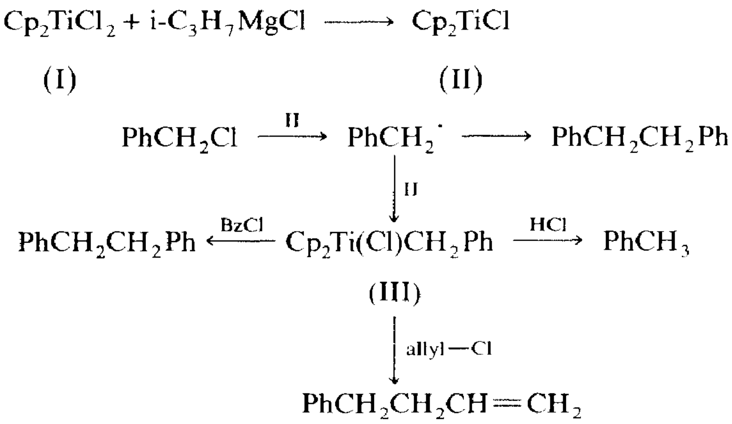
[a] The molar ratio of Cp_2TiX to benzylic and allylic halides is 1/1 (based on one halogen atom); while that of Cp_2TiCl to α-bromoketones is 2/1. [b] A stands for isolated Cp_2TiCl from Cp_2TiCl_2 + Al; B and C stand for Cp_2TiCl and Cp_2TiBr in situ from Cp_2TiCl_2 + i-C_3H_7MgCl and Cp_2TiCl_2 + i-C_3H_7MgBr, respectively. [c] Isolated yield unless indicated. [d] Detected by GLC.



Scheme 1. The reaction of BzCl and Cp_2TiCl.

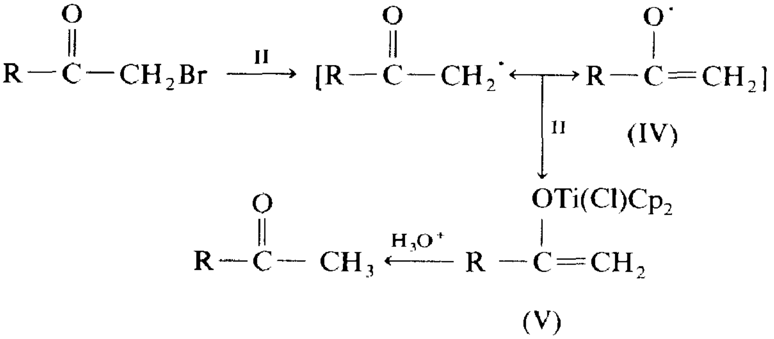
Reactions of Cp_2TiCl with benzal chloride and benzotrichloride in the molar ratios of 2/1 and 3/1 produce *trans*-stilbene and tolan respectively.

α-Bromoketones are also reactive towards dicyclopentadienyltitanium chloride. They differ from benzylic and allylic halides by requiring two moles of Cp_2TiCl per mole of the α-bromoketones to complete the reactions. The first mole of Cp_2TiCl possibly abstracts the bromine atom of the α-bromoketone and the resulting radical IV combines with the second mole of Cp_2TiCl 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 $PhCH_2CH_2Cl$, EtBr and PhBr fail to react with Cp_2TiCl. In this connection, Cp_2TiCl differs from Cp_2TiCl_2/Mg [12] and vanadocene [21,22].

Experimental

Ether and tetrahydrofuran were dried over Na–Ph_2CO and degassed before distillation. NMR spectra were recorded on a Varian EM-360A (60 MHz) NMR Spectrometer using 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 α-bromoketones by Cp_2TiCl.

Typical procedures are as follows: Preparation of Cp_2TiCl. To Cp_2TiCl_2 (1.0 g) in 5 ml of THF was added 4 ml of i-C_3H_7MgCl (1.0 *M* in Et_2O) under argon atmosphere. The resulting mixture was stirred at room temperature for 0.5 h. The green Cp_2TiCl so-formed was used without isolation in the following reactions.

Reaction of BzCl with Cp_2TiCl. Benzyl chloride (0.46 ml, 4 mmol) was added to Cp_2TiCl (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 Cp_2TiCl_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 BzCl using catalytic amount of Cp_2TiCl_2. BzCl (0.23 ml, 2 mmol) was added to Cp_2TiCl (2 mmol). After 5 h, 2.0 ml of i-C_3H_7MgCl (2 mmol) was added to the red reaction mixture and stirred for 0.5 h. Then 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. ^1H NMR showed it was composed of 74% of dibenzyl and 26% of BzCl (in weight), corresponding to 81% total conversion of BzCl.

Cross coupling of BzCl and allyl–Cl. BzCl (0.23 ml, 2 mmol) was added to Cp_2TiCl. 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, $PhCH_2CH_2CH{=}CH_2$ and diallyl was 35/32/33.

Reaction of $PhCHCl_2$ with Cp_2TiCl. Benzalchloride (0.25 ml, 2 mmol) was added to Cp_2TiCl (4 mmol). After the usual work-up, the crude product was recrystallized from $EtOH/H_2O$ to give 30 mg of *trans*-stilbene in 17% yield.

Reaction of 2,4′-dibromoacetophenone with Cp_2TiCl. 2,4′-dibromoacetophenone (556 mg) in THF (5 ml) was added to Cp_2TiCl (4 mmol) and the resulting red mixture was stirred at room temperature for 5 h. Then 2*N* HCl (5 ml) and petroleum (50 ml) was added. The petroleum solution was separated from the filtrate, dried over Na_2SO_4 and concentrated to give crystalline solid (340 mg) in 85% yield.

Acknowledgement

Financial support from the Foundation of National Natural Science of China is gratefully acknowledged.

References

1 M.L.H. Green, C.R. Lucas, J. Chem. Soc. Dalton Trans., (1972) 1000.
2 R.S.P. Coutts, P.C. Wailes, R.L. Martin, J. Organomet. Chem., 47 (1973) 375.
3 G. Natta, G. Dall'asta, G. Mazzanti, U. Giannini, Angew, Chem., 71 (1959) 205.
4 L.E. Manzer, D. Sekutowski, G.D. Stucky, Inorg. Chem., 14 (1975) 2192.
5 R. Jungst, D. Sekutowski, J. Davis, M. Luly, G.D. Stucky, Inorg. Chem., 16 (1977) 1645.
6 R.S.P. Coutts, J.R. Sturtees, Aust. J. Chem., 19 (1966) 387.
7 A. Dormond, T. Kolavudh, J. Tirouflet, C.R. Hebd. Seances Acad. Sci., Sér. C., 282 (1976) 551.

8 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, B. Wolf, U. Thewalt, J. Organomet. Chem., 297 (1985) 159.
9 K.B. Bottomley, H.H. Brintzinger, J. Chem. Soc. Chem. Commun., (1978) 234.
10 G. Fachinetti, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Am. Chem. Soc., 101 (1979) 1767.
11 W.A. Nugent, T.V. RajanBabu, J. Am. Chem. Soc., 110 (1988) 8561.
12 T.R. Nelsen, J.J. Tufariello, J. Org. Chem., 40 (1975) 3159.
13 E.C. Ashby, J.J. Lin, J. Org. Chem., 43 (1978) 1263.
14 T. Mukaiyama, M. Hayashi, K. Narasaka, Chem. Lett., (1973) 291.
15 G.A. Olah, G.K.S. Prakash, Synthesis, (1976) 607.
16 A. Merijamanian, T. Mayer, J.F. Helling, F. Klemick, J. Org. Chem., 37 (1972) 3945.
17 H.A. Martin, F. Jellinek, J. Organomet. Chem., 12 (1968) 149.
18 J.A. Waters, G.A. Mortimer, J. Organomet. Chem., 22 (1970) 417.
19 J.A. Waters, V.V. Vickroy, G.A. Mortimer, J. Organomet. Chem., 33 (1971) 41.
20 C.P. Gibson, G. Dabbagh, S.H. Bertz, J. Chem. Soc. Chem. Comm., (1988) 603.
21 R. Sustmann, G. Kopp, J. Organomet. Chem., 347 (1988) 328.
22 R. Sustmann, G. Kopp, J. Organomet. Chem., 347 (1988) 313.
23 Qian Yanlong, Li Guisheng et al., J. Mol. Catal., to be published.