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Isomerization of terminal alkenes by the $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ system

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Abstract

The reagents prepared in situ in tetrahydrofuran (THF) by reaction of Cp_2TiCl_2 with isobutyl or t-butylmagnesium halides or with Grignard grade magnesium and 1,2-dibromoethane bring about isomerization of some 1-alkenes into *trans*-2-alkenes under mild conditions.

Introduction

During our study on the development of hydrometallation routes to transition metal organometallics [1,2], it became of interest to explore the possibility of using hydrotitanation of 1-alkenes, followed by transmetallation of the resulting organotitanium species with MgX_2, to obtain the corresponding organomagnesium compounds. This has been achieved previously by treatment of 1-alkene with isobutylmagnesium bromide in the presence of catalytic amount of Cp_2TiCl_2 under argon [3]. However, we have found that when 1-decene (10 mmol) is added to a mixture containing isobutylmagnesium bromide (12 mmol) and Cp_2TiCl_2 (2 mmol) in THF (80 ml) at room temperature under nitrogen and the reaction mixture is stirred for 2 h then hydrolysed, only a mixture of *trans*-2-decene and *cis*-2-decene (~ 85/15) [4*] (in 75% yield) is obtained, and no decane is formed (Table 1). This indicates that the Cp_2TiCl_2/iso-BuMgBr system under nitrogen isomerizes 1-alkenes and does not give the Cp_2TiH species that is capable of catalyzing the hydrotitanation-transmetallation to give the corresponding 1-decylmagnesium bromide.

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* Reference number with asterisk indicates a note in the list of references.

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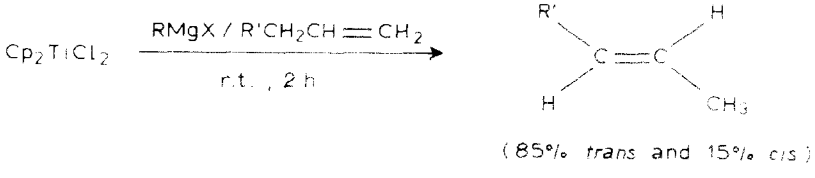


(R = iso-butyl or t-butyl ; R' = n-C_7H_{15})

We have observed that the Cp_2TiCl_2/t-BuMgCl system also isomerizes 1-decene into *trans*-2-decene and *cis*-2-decene (~ 85/15) in 75% yield under nitrogen (Table 1). It was previously reported that the Cp_2TiCl_2/t-BuMgCl system under argon isomerizes 1-octene to *trans*-2-octene and *cis*-2-octene, and evidence was presented for the presence of Cp_2Ti(t-Bu) species in the reaction mixture. We were intrigued by the differences between the reactivity of Cp_2TiCl_2/iso-BuMgX under argon and under nitrogen, and decided to investigate further.

An earlier report indicated the formation of $[Cp_2Ti]_2N_2$ complex in the reaction of Cp_2TiCl_2 with iso-propylmagnesium bromide in THF [5]. The reaction of the $[Cp_2Ti]_2N_2$ prepared in this way with 1-alkenes has not been explored [6*,7]. However, the ethylene complex, bis(pentamethylcyclopentadiene)titanocene, $[C_5(CH_3)_5]_2Ti(CH_2{=}CH_2)$, has been reported to catalyze isomerization of 1-hexene, primarily to *trans*-2-hexene [8]. We decided to prepare and explore the reactivities of such titanocene complexes with 1-alkenes using some other reagent system in order to compare with the Cp_2TiCl_2/RMgX system.

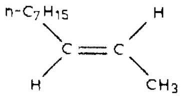
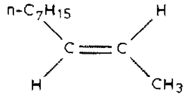
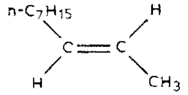
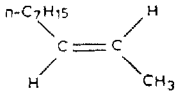
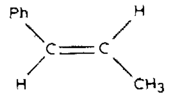
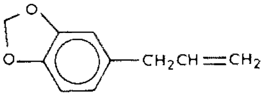
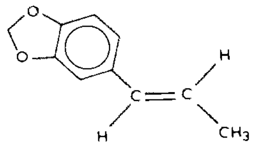
Results and discussion

A number of reagents have been shown to reduce Cp_2TiCl_2 into titanocene, 'Cp_2Ti' or its equivalent (i.e. its dimer or N_2 or solvent complex) [9–16]. The simplest of these reagents appeared to be the one involving Cp_2TiCl_2 and magnesium in THF [15]. However, we observed that when 1-decene (10 mmol) was added to Cp_2TiCl_2 (2 mmol) and Grignard-grade magnesium (25 mmol) and the mixture stirred for 2 h at room temperature the 1-decene remained unchanged. Also, there is no indication of reduction of the orange-coloured Cp_2TiCl_2 to the low valent titanium species [15]. However, when 1,2-dibromoethane (25 mmol) was utilized to activate the magnesium [17*,18], the colour of the mixture changed from orange to dark green during 30 min. We observed that the titanium species prepared from Cp_2TiCl_2, magnesium and 1,2-dibromoethane in THF isomerizes 1-decene to *trans*-2-decene and *cis*-2-decene (~ 85/15) in 78% yield (Table 1). Control experiments indicate that 50 mmol of 1-decene can be converted into a mixture of *trans*-2-decene and *cis*-2-decene (85/15) in 12 h at room temperature (Table 1).

Allylbenzene and safrole were converted into the corresponding *trans*-β-methylstyrenes in 77 and 80% yields, respectively (Table 1). *Cis,cis*-1,5-cyclooctadiene, which undergoes conjugation to give *cis,cis*-1,3-cyclooctadiene with several isomerization catalysts [19], is not affected by the present reagent, and neither is limonene. These results indicate that the titanocene-equivalent prepared by our method shows promise for use in the selective isomerization of monosubstituted olefinic moiety in the presence of disubstituted and trisubstituted olefinic groups. The inertness of

Table 1

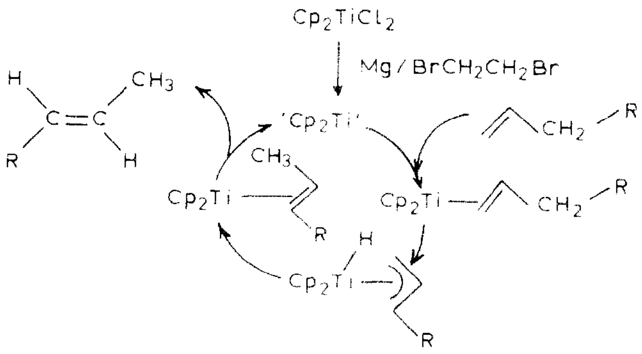
Isomerization of 1-alkenes

1-Alkene	Reagent system (Cp_2TiCl_2 and)	Reaction time (h)	Product [d]	Yield
n-$C_7H_{15}CH_2CH=CH_2$	$CH_3CH(CH_3)CH_2MgX$ [a]	2		75 [e]
n-$C_7H_{15}CH_2CH=CH_2$	$(CH_3)_3CMgX$ [a]	2		75 [e]
n-$C_7H_{15}CH_2CH=CH_2$	$BrCH_2CH_2Br/Mg$ [b]	2		78 [e]
n-$C_7H_{15}CH_2CH=CH_2$	$BrCH_2CH_2Br/Mg$ [c]	12		75 [e]
$PhCH_2CH=CH_2$	$BrCH_2CH_2Br/Mg$ [b]	2		77 [f]
	$BrCH_2CH_2Br/Mg$ [b]	2		80 [g]

[a] The reactions were carried out at room temperature under nitrogen by use of Cp_2TiCl_2 (2 mmol), the Grignard reagent prepared from Mg (25 mmol), alkyl bromide (12 mmol), and 1-alkene (10 mmol). [b] The reactions were carried out with Cp_2TiCl_2 (2 mmol), 1,2-dibromoethane (25 mmol), Mg (25 mmol), and 1-alkene (10 mmol). [c] The reaction was carried out with 50 mmol of 1-decene. Other reagents were taken in quantities given under note *b*. [d] The products were isolated by column chromatography (silica gel with hexane as eluant) and identified by their IR and ^{13}C NMR spectral data and comparison with literature data (Ref. 19). [e] The *trans/cis* ratio ~ 85/15 (see Experimental [4*]. [f] 100% *trans* product: ^{13}C NMR signals ($CDCl_3$, δ 0 ppm for TMS): 138.5, 131.9, 129.0, 127.3, 126.4, 125.7 and 19.7. [g] 100% *trans* product: ^{13}C NMR signals ($CDCl_3$, δ 0 ppm for TMS): 148.3, 146.9, 132.7, 131.1, 123.6, 120.4, 108.3, 105.5, 101.1 and 19.2.

disubstituted olefins towards the reagent is also indicated by the absence of 3-decenes and 4-decenes in the isomerization of 1-decene into 2-decenes.

It has been shown that Cp_2TiCl_2 and Cp_2TiCl do not isomerize alkenes [3]. The complex, $(C_5H_5)_3(C_5H_4)Ti_2$, prepared by reducing Cp_2TiCl_2 with potassium naph-



Scheme 1

thalenide in THF at −80 °C, catalyzes rapid isomerization of 1-heptene to *trans*-2-heptene ($\sim$ 95%) and *cis*-2-heptene ($\sim$ 5%) [20]. This reagent also catalyzes rapid isomerization of *cis,cis*-1,5-cyclooctadiene, in contrast to the present reagent system. The $[C_5(CH_3)_5]_2Ti(CH_2{=}CH_2)$ system has been reported to isomerize 1-hexene into primarily *trans*-2-hexene but in that system the $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiH$ species was shown to be the catalyst [8]. Although the reactive species in the present reagent system may not be simply 'Cp_2Ti', the isomerization may be tentatively visualized in terms of the mechanism involving a 1,3-hydride shift assuming the intermediacy of 'Cp_2Ti' or its equivalent and the formation of Cp_2Ti-olefin complexes (Scheme 1).

The titanocene equivalents have been utilized in the fixation of nitrogen [21] and for the preparation of the corresponding metallocycles [22]. Theoretical calculations predicted carbene-like character for titanocene [23,24]. Accordingly, the present simple method of generating titanocene or its equivalent would make these species readily accessible for synthetic use.

Experimental

The THF was distilled from benzophenone-sodium immediately before use. The dichlorobis(cyclopentadiene)titanium(IV), Cp_2TiCl_2 supplied by Fluka, Switzerland was used. The alkenes were commercial samples. Grignard grade magnesium was used.

Reaction of 1-decene with the Cp_2TiCl_2/isobutylmagnesium bromide system

Iso-butylmagnesium bromide was prepared in THF (60 ml) using iso-butyl bromide (12 mmol) and magnesium (20 mmol) at room temperature under nitrogen. A solution of dichlorobis(cyclopentadiene)titanium(IV) (2 mmol) in THF (60 ml) was made up under nitrogen atmosphere and the iso-butylmagnesium bromide solution was then transferred into it through a cannula under nitrogen. After 30 min 1-decene was injected and the mixture was stirred for 2 h at room temperature. The mixture was hydrolysed with 5*N* HCl (50 ml) and extracted with ether (3 × 30 ml). The combined organic extract was washed with water (50 ml) and saturated aqueous NaCl (50 ml) and then dried over $MgSO_4$. The solvent was evaporated and the residue chromatographed on a silica gel column with hexane as eluent.

^{13}C NMR data (in ppm, $\delta = 0$ TMS) for *trans*-2-decene: 131.6, 124.4, 32.6, 31.9, 29.7, 29.2, 22.6, 17.5 and 13.8; in addition the product gave signals at 130.7, 123.4, 26.8 and 12.7, characteristic of *cis*-2-decene [14]. The ratio of *trans*/*cis*-2-decene was found to be ca. 85/15 by integration of the olefinic carbon signals [4*].

Representative procedure for isomerization using $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ *system*

1,2-Dibromoethane (15 mmol) was added during 10 min at room temperature under nitrogen to a THF solution (80 ml) of dichlorobis(cyclopentadiene)titanium(IV) (2 mmol) in the presence of Grignard-grade magnesium (20 mmol). The mixture turned dark green within 30 min. Allylbenzene (10 mmol) was added and the mixture was stirred for 2 h at room temperature then hydrolyzed with 5*N* aqueous HCl (50 ml) and extracted with ether (3 × 30 ml). The combined extracts were washed with water (50 ml) and saturated aqueous NaCl (50 ml) then dried over $MgSO_4$. The solvent was evaporated off, and the residue chromatographed on a silica gel column with hexane as eluent. The product was pure *trans*-β-methylstyrene: ^{13}C NMR data (in $CDCl_3$, TMS $\delta = 0$ ppm): 138.5, 131.9, 129.0, 127.3, 126.4, 125.7 and 19.7.

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4 The ratios of *trans*/*cis* isomers of 2-decenes reported are only approximate as they are based on the relative intensities of the olefinic carbon signals which are affected by NOE. We previously reported [Ref. 19] a *trans*/*cis* isomer ratio of 90/10 for the mixture of *trans*/*cis*-2-decenes on the basis of relative intensities of the proton signals in the 270 MHz spectrum of the CH_3 groups attached to the olefinic moieties. Comparison of the relative intensities of the olefinic carbon signals obtained in that case [Ref. 19] with that obtained for the *trans*/*cis*, isomers obtained in the present procedure indicates that the ratio is closer to 85/15.
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6 We thank a referee for drawing our attention to a report [Ref. 7] that a solid material, considered to be a titanocene equivalent, prepared by evaporation of the solvent from the reaction mixture of the Cp_2TiCl_2/i-PrMgBr in diethyl ether, isomerises neat 1-hexene to a mixture of *trans* 2-hexene, *cis*-2-hexene, and *trans*-3-hexene in the ratio of 51/29/20. Under our conditions, 1-decene does not give any 3-decene or 4-decene, and so the new method gives a more selective transformation. The differences in the reactivities indicate that the active species and mechanism may also be different. We have rationalised the present transformations in terms of the tentative mechanism given in Scheme 1 taking into account the carbene-like character predicted for titanocene [Ref. 23, 24]. Nakamura and coworkers [Ref. 7] considered the possibility of involvement of Cp_2TiH for their Cp_2TiCl_2/i-PrMgBr system.

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17 1,2-Dibromoethane is frequently used for activating magnesium in Grignard reactions [Ref. 18]; produces $MgBr_2$ and ethylene and continuously cleans the surface of the magnesium. A referee has pointed out that 1,2-dibromoethane *may* have a much more active role in our system. It is possible that under the present reaction conditions the titanocene ethylene complex $Cp_2Ti(CH_2{=}CH_2)$ is formed, since it is known [Ref. 14] that ethylene reacts with titanocene generated by the reduction Cp_2TiCl_2 with $LiC_{10}H_8$ at -50 °C and on carbonylation gives 17% of cyclopentanone. However, we have observed that when the titanocene equivalent was prepared at room temperature using $Mg/BrCH_2CH_2Br$ system as described in experimental section and carbonylation was carried out at -50 °C, no carbonyl compound was formed.

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