Catalysis Letters Vol. 72, No. 1-2, 2001

Isomerization and anti-Markovnikov arylation of olefin catalyzed by an iridium complex

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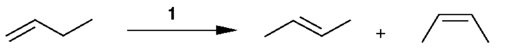
Received 5 October 2000; accepted 5 December 2000

An iridium acetylacetonato complex, a catalyst for anti-Markovnikov arylation of olefins, was found to work as a catalyst for olefin isomerization. 2-butene was obtained with 0.55 *cis*/*trans* ratio in isomerization of 1-butene. Moreover, in 1-hexene/benzene solution, isomerization and arylation of 1-hexene were simultaneously catalyzed by the iridium complex.

KEY WORDS: iridium; homogeneous; catalyst; isomerization; anti-Markovnikov; arylation; CH activation

We have reported the anti-Markovnikov arylation of olefins catalyzed by a binuclear Ir(III) complex, [Ir(μ-acac-O,O$'$,C^3)(acac-O,O$'$)(acac-C^3)]$_2$ (acac = acetylacetonato) **1**, to produce straight-chain alkylbenzene in higher selectivity than branched alkylbenzene [1]. For example, n-propylbenzene was produced in 61% selectivity by alkylation of benzene with propylene. This type of reaction, which employs unsubstituted benzene, is quite new. Although the mechanism of the reaction is not yet clear, we propose that the reaction occurs via CH activation of benzene by the Ir center. As a relevant reaction, alkylations of aromatic ketones and olefins catalyzed by Ru complexes were reported [2]. In view of the unusual selectivity of products, exploitation of catalysis through C–H bond activation is attractive.

We found that the isomerization of 1-hexene simultaneously occurred in the anti-Markovnikov arylation of 1-hexene. Herein we report the isomerizations of various olefins catalyzed by complex **1** and discuss the isomerization and the arylation of 1-hexene. The comparison study of reaction conditions and catalysts for isomerization of 1-butene (equation (1)) is shown in table 1 (entries 1–7).



(1)

The typical reaction procedure is as follows: a 10 ml steel autoclave equipped with a glass insert and a magnetic stir bar was charged with 3 ml of n-heptane and 1.3 mg of **1**. The reactor was degassed with N_2, pressurized with 0.10 MPa of 1-butene, sequentially pressurized with CO_2 up to 0.20 MPa, followed by pressurization with N_2 up to 1.96 MPa, and heated to 180 °C with stirring for 10 min. The gas phase was sampled and analyzed by GC (TCD), and the liquid phase was analyzed by GC (FID) at the end of the reaction. 1-butene was isomerized by **1** at 180 °C to afford *cis*- and *trans*-2-butene in 0.55 ratio (TOF $= 167 \times 10^{-3}\ \mathrm{s}^{-1}$; entry 1).

Two kinds of mechanisms for olefin isomerization by group VIII complexes are well documented [3–10]: the first goes via alkyl intermediates; the second is by π-allyls. In the alkyl route, a metal–hydride bond and insertion of olefin into the bond are required. Since complex **1**, which is assumed to be a monomer in the reaction, does not have a hydride, the isomerization appears to occur through the latter mechanism, the π-allyl route. Therefore, we propose the following possible mechanism. Complex **1**, Ir(III), is reduced to Ir in a lower oxidation state in the reaction followed by CH bond activation at the allylic position of 1-butene through the oxidative addition to an Ir center, and then 1-butene and 2-butene are afforded by dint of the reductive elimination.

In the isomerization of 1-butene catalyzed by base catalysts, π-allyl anionic intermediates are employed. Because of the high stability of the *cis*-π-allyl anion (anti-), the *cis*/*trans* ratio is larger than 1.0, sometimes higher than 20 [11–16]. The isomerization by group VIII complexes is in contrast to the base catalysis despite close forms of activated olefins, π-allylic intermediates.

$H_3PW_{12}O_{40}$ as a typical Brønsted acid, Ir(acac)(CO)$_2$ **2** and [Ir(COD)Cl]$_2$ (COD = cyclooctadiene) **3**, in Ir(I) oxidation state, were also used for the isomerization of 1-butene. In order to compare the *cis*/*trans* ratio and TOF in lower conversion, in which the reaction has not reached equilibrium, a temperature of 160 °C was employed (entries 2 and 5–7). Complexes **2** and **3** showed close performances to **1** regarding TOF (entries 2, 6 and 7). However *cis*/*trans* ratios in **2** and **3** were much lower than in **1**. TOF with $H_3PW_{12}O_{40}$ was smaller than that with **1**. Furthermore, at 180 °C some olefin oligomers were observed in the $H_3PW_{12}O_{40}$ case.

Various olefins were also examined for the isomerization catalyzed by complex **1**. 2-hexene (*cis* and *trans*) and 3-hexene (*cis* and *trans*) were formed in the isomerization of 1-hexene. *Cis*/*trans* ratio in 2-hexene was less than 1.0, the

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Table 1
Isomerization of various olefins.

Entry	Reaction media		Catalyst	Conditions	*Cis*/*trans* ratio	Conversion[a] (%)	TN[b]	TOF[b] ($\times10^{-3}$ s^{-1})
	Olefin	Solvent						
1	1-butene	*n*-heptane	**1**	180 °C, 10 min	0.55	78	101	167
2	1-butene	*n*-heptane	**1**	160 °C, 10 min	0.69	26	36	59
3	1-butene	Benzene	**1**	160 °C, 10 min	0.32	37	50	83
4	1-butene	*n*-heptane	HPA[c]	180 °C, 10 min	0.77	21	15	25
5	1-butene	*n*-heptane	HPA[c]	160 °C, 10 min	0.85	10	8	14
6	1-butene	*n*-heptane	**2**	160 °C, 10 min	0.29	35	32	53
7	1-butene	*n*-heptane	**3**	160 °C, 10 min	0.15	41	47	78
8	1-hexene[d]	*n*-heptane	**1**	180 °C, 20 min[e]	0.50[f]	47	846	705
9	1-hexene[d]	Benzene	**1**	180 °C, 20 min[e]	0.49[f]	46	991	826
10	1-hexene[d]	–	**1**	180 °C, 20 min[e]	0.51[f]	14	1103	919
11	23DMB[d,g]	*n*-heptane	**1**	180 °C, 20 min[e]	–	6	90	75
12	23DMB[d,g]	Benzene	**1**	180 °C, 20 min[e]	–	8	122	102
13	23DMB[d,g]	–	**1**	180 °C, 20 min[e]	–	4	286	238
14	5VNB[d,h]	–	**1**	180 °C, 20 min[e]	–	0	0	0

[a] Conversion of starting olefin to isomers.
[b] TN and TOF are based on Ir for **1**, **2** and **3**.
[c] $H_3PW_{12}O_{40}$.
[d] 1.7 M of olefin.
[e] Pressurization with 2.94 MPa of N_2.
[f] *Cis*/*trans* ratio in 2-hexene.
[g] 2,3-dimethyl-1-butene.
[h] 5-vinyl-2-norbornene.

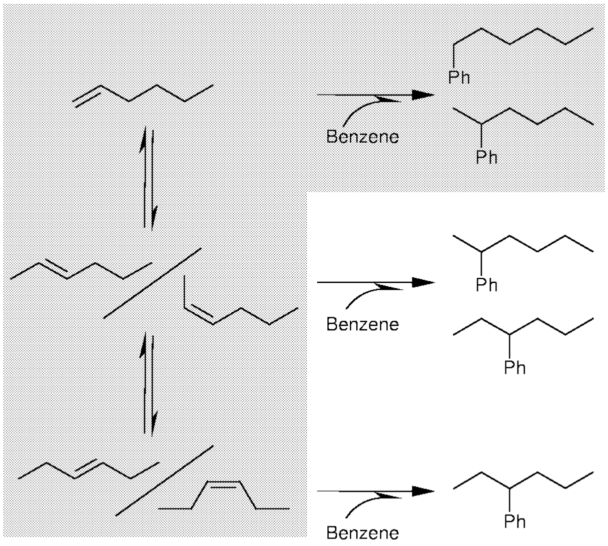
Table 2
Isomerization and arylation of 1-hexene catalyzed by **1**.[a]

Entry	Benzene/1-hexene ratio	Isomerization				Arylation			
		TOF[b] ($\times10^{-3}$ s^{-1})	Composition of hexene (%)			TOF[b] ($\times10^{-3}$ s^{-1})	Composition of phenylhexane (%)		
			1-hexene	2-hexene	3-hexene		1-PhHx[c]	2-PhHx[d]	3-PhHx[e]
15	5	826	54	39	7	6.9	69	31	0
16	10	665	7	75	18	8.9	67	33	0
17	15	631	9	73	18	8.3	67	33	0

[a] Pressurization with 2.94 MPa of N_2. Reactions were proceeded at 180 °C for 20 min.
[b] TN and TOF are based on Ir.
[c] 1-phenylhexane.
[d] 2-phenylhexane.
[e] 3-phenylhexane.

same as for 1-butene, but no difference in the reaction media was observed with respect to *cis*/*trans* ratio (entries 8–10). Isomerization of 2,3-dimethyl-1-butene having a tertiary carbon atom at one of the allylic positions was also observed to afford 2,3-dimethyl-2-butene (entries 11–13). However, the TOF was significantly smaller than that of 1-hexene. On the other hand, interestingly 5-vinyl-2-norbornene (mixture of *endo* and *exo*) was not isomerized by **1** probably because of steric hindrance.

In the reaction of benzene with 1-hexene, the isomerization and the arylation of 1-hexene occurred simultaneously. Table 2 shows results of the reactions in various benzene/1-hexene ratios. In all cases, the reaction rates of isomerization were almost two orders of magnitude faster than that of arylation. At the end of the reaction, a large amount of 1-hexene was isomerized to 2-hexene, and especially in entries 16 and 17, 2-hexene accounted for almost 75% in the hexene composition. As shown in scheme 1, 2-phenyl-



Scheme 1

hexane and 3-phenylhexane could be afforded by the arylation of 2-hexene, and 3-phenylhexane could be obtained from 3-hexene. However, the production of 3-phenylhexane was not observed at all, suggesting that the arylations of 2-hexene and 3-hexene were fairly slow compared to the arylation of 1-hexene. Furthermore, almost the same ratios of 1-phenylhexane/2-phenylhexane were observed in entries 15 and 16 in spite of different compositions of hexene. Accordingly, this suggests that the product ratio, 1-phenylhexane/2-phenylhexane, was determined only by the arylation of 1-hexene even though other isomers were produced *in situ*.

In summary, we report olefin isomerizations catalyzed by the iridium complex **1** via oxidative addition of olefin to an Ir center. Moreover, in the reaction of 1-hexene with benzene, the isomerization of 1-hexene showed a reaction rate almost hundred-fold faster than the arylation of 1-hexene. In the composition of hexene, 1-hexene was dominant for the arylation.

Acknowledgement

We thank the staff of Catalytica Advanced Technologies, Inc. for discussion.

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