Journal of Organometallic Chemistry, 327 (1987) C1–C4
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Thermal and photochemical olefin isomerizations with complex $[(C_5Me_4H)_2Ti(CH_3)_2]$ as initiator

P. Courtot, R. Pichon, Y. Raoult and J.Y. Salaün

Laboratoire de Photochimie, Electrochimie et Chimie Moléculaire de l'Université de Bretagne Occidentale, Associé au CNRS (UA 322), 6, avenue le Gorgeu, 29287 Brest Cédex (France)

(Received February 9th, 1987)

Abstract

Irradiation of the complex $[(C_5Me_4H)_2Ti(CH_3)_2]$ in an olefin as a solvent promotes stereospecific photoassisted isomerizations: olefins with terminal double bonds are rapidly isomerized into 2-alkenes with an *E*-configuration. Kinetic studies of hydrogen migrations and of *Z*-*E* isomerizations of disubstituted olefins have demonstrated the influence of substitution and of branching of the hydrocarbon chain on the course of the reaction. Formation of paramagnetic complexes of Ti^{III} that are probably intermediates in these reactions has been confirmed by ESR. The same reactions, but with a lower stereoselectivity, are initiated thermally by the $[(C_5Me_4H)_2Ti(CH_3)_2]$ complex.

Catalysis of olefin isomerizations by titanium complexes derived from $[Cp_2TiCl_2]$ have been recently reported [1–5]. However, though several examples of thermal catalysis have been documented, there are very few examples of photochemical initiation. In the course of a study of photocatalytic olefin hydrogenation, Samuel [6] referred to an isomerization of the olefins upon irradiation of complexes of the type $[Cp_2TiR_2]$ ($R = CH_3$, CH_2Ph, Ph) in the presence of hydrogen.

We became interested by the possible photochemical formation of Ti^{III} or even Ti^{II} complexes by homolytic metal–carbon bond rupture, a well-known reaction in the field of photochemistry of transition-metal complexes [7–12]. We describe here the use of a new titanium complex, $[(C_5Me_4H)_2Ti(CH_3)_2]$ (**1**), prepared in our laboratory [13], in the initiation of olefin isomerizations.

As our titanium complex is conveniently soluble in hydrocarbons, we were able to irradiate deoxygenated solutions of one complex equivalent dissolved in 400 olefin equivalents ($\simeq 1.95 \times 10^{-5}$ *M*) with a Philips HPK 125 mercury lamp emitting above 310 nm. The photoisomerizations were monitored by NMR and GLC (30% PPG column-12 m).

0022-328X/87/$03.50

The first group of alkenes studied consisted of 1-pentene, 1-hexene, 1-octene, and 1-decene. Irradiation of the $[(C_5Me_4H)_2Ti(CH_3)_2]$ complex in these olefins leads to hydrogen migration along the hydrocarbon chain to yield selectively 2-unsaturated olefins. Isomerization reaches 99% of the starting material after 3 h of irradiation. The reactions are stereospecific if the irradiation is stopped immediately after disappearance of the initial olefin; at this stage the following proportions are found: 97% of *E*-2-pentene, *E*-2-hexene, *E*-2-octene or *E*-2-decene, 2% of the *Z*-2-isomers and 1% of the initial olefin. Other possible isomers such as 3-hexene, 3- or 4-octenes, and 3-, 4- or 5-decenes have not been detected after the irradiation.

Kinetic studies allowed us to detect an induction period involving a slow isomerization (10% of olefin is transformed during 1 h and 40 min of irradiation). The studies also show that the reaction is a photoassisted rather than a photocatalyzed process: it stops as soon as the irradiation is interrupted, but it may start again, without an induction period after several hours or several days without observable change when the solutions are kept in the dark.

The formation and the transformation of titanium(III) paramagnetic complexes were monitored by ESR spectroscopy. Figure 1 shows the behaviour when complex **1** is irradiated in 1-hexene. Only one signal is present after the solution has been irradiated for 30 s; it is a broad singlet with 8 satellites characteristic of a Ti^{III} complex ($g = 1.979$; ΔH 3.4 G and A(Ti) 7.45 G). Prolonged irradiation leads to the appearance of two other broad signals ($g = 1.992$ and $g = 1.973$), the low field one largely predominating after 1 h and 40 min irradiation. As the increase in the broad signal ($g = 1.992$ and ΔH 6 G) parallels the increase in the isomerization rate, we believe that a Ti^{III} complex characterized by this signal could be involved in the isomerization. The ESR characteristics (g-value, ΔH) of such Ti^{III} intermediates are very similar to those attributed to $[(Cp_2Ti(\eta^3\text{-allyl})]$ complexes [14–16]. Work is in progress to prepare and isolate such complexes.

Olefins with a branched chain undergo slower isomerization than linear olefins. The irradiation of $[(C_5Me_4H)_2Ti(CH_3)_2]$ was examined for solutions in 2-methyl-, 3-methyl-, or 4-methyl-1-pentenes. For the two first olefins, the isomerization yields are very low: less than 5% of 2-methyl-2-pentene and 3-methyl-2-pentene, respectively, are present even after 30 h of irradiation. The behaviour of 4-methyl-1-pentene is intermediate between that of branched and linear olefins. The reaction is complete after 15 h of irradiation and the formation of 97% of *E*-4-methyl-2-pentene shows the very high stereospecificity of the hydrogen migration. The ESR spectra observed in monitoring the reaction are complex, but there is a broad signal at low field ($g = 1.992$), which is weak compared to that of the signal obtained when the irradiation is performed in 1-pentene, 1-hexene, or 1-octene.

These results show that isomerization processes are strongly influenced by the position of branching of the chain of the olefin. Migration is almost inhibited when a methyl group is present on the double bond or in an allylic position, and the reaction takes place very slowly in the case of 4-methyl-1-pentene.

Irradiations of the complex $[(C_5Me_4H)_2Ti(CH_3)_2]$ in the presence of disubstituted olefins provide information on the remarkable stereospecificity observed for the reaction of the mono-substituted olefins previously described. Prolonged irradiation either of a solution of 97% *E*-2-isomer and 2% of *Z*-2-isomer of olefins obtained as described above by irradiating 1-olefins, or of a solution of the pure *E*-2 or *Z*-2-isomers (2-pentene, 2-hexene, 2-octene), produce only slow photoassisted

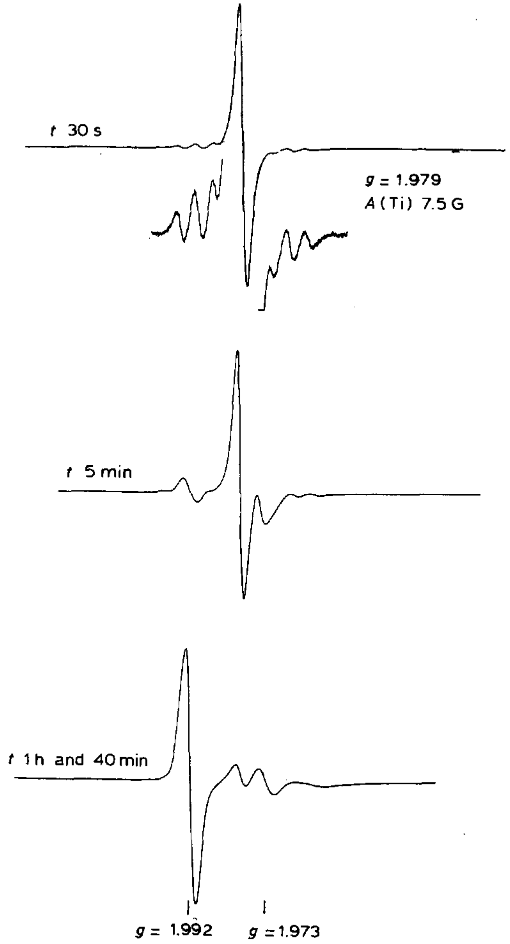

Fig. 1. Changes in the ESR spectra of irradiated solutions of $[(C_5Me_4H)_2Ti(CH_3)_2]$ in 1-hexene.

Z-*E* isomerizations of the double bonds, and there is no hydrogen migration to any position. After 35 to 40 h of irradiation, photostationary mixtures of *E*-2 and *Z*-2 isomers are present in an 80/20 ratio (the proportion corresponding to a thermodynamic equilibrium), whatever the configuration of the initial olefin. Olefins with the double bond at carbon-3, such as 3-hexene, show no appreciable isomerization under these conditions even after longer irradiation times: after 60 h there is 95% of the initial *E*-3-hexene, 3% of *E*-2 and 1% of *Z*-2-hexene and only traces of *Z*-3-hexene.

The complex $[(C_5Me_4H)_2Ti(CH_3)_2]$ also promotes thermal isomerization of the olefins similar to the photochemical process. The reactions were performed with 1.95×10^{-5} *M* solutions of the complex in olefin. The thermal isomerization in the case of terminal olefins (1-pentene, 1-hexene, and 1-octene) involves a stereoselective double bond migration to carbon-2 after an induction period of about 3 h. The reaction is complete after 7 h at 130 °C. If the reaction is stopped after the disappearance of the initial olefin, a mixture consisting of 97% of the *E*-2-isomer, 2% of the Z-2-isomer, and 1% of the initial olefin is present (the proportions being similar to that in the mixture obtained by the photochemical process). The results are quite different, however, in the case of di-substituted olefins: isomerization of *E*-2-hexene yields after 14 h at 130 ° C a mixture of 21% *Z*-2-hexene, 66% *E*-2-hexene and 13% *Z*-3-hexene, whereas only *Z*-*E* isomerization was observed upon irradiation. With *E*-3-hexene, both migration and *Z*-*E* isomerization are observed in the thermal process (55% *E*-3-hexene, 33% *E*-2-hexene and 11% *Z*-2-hexene after 14 h at 130 ° C), whereas the olefin was practically unreactive under irradiation.

Photochemical transformations of terminal olefins in the presence of $[(C_5Me_4H)_2Ti(CH_3)_2]$ exhibit a remarkable stereoselectivity: the only reaction observed is the hydrogen migration to give an olefin with the double bond with the *E* configuration on carbon-2. Under the same conditions these olefins undergo only a slow *E*-*Z* isomerization of the double bond without any migration of hydrogen along the carbon chain. The thermal activation of terminal olefins gives the same stereoselectivity as the photochemical process. Olefins with double bond on carbon-2 undergo an *E*-*Z* isomerization and a double bond migration to give a complex mixture of isomers.

We are at present directing our studies to identification of intermediate complexes involved in these photochemical and thermal isomerizations, and the influence of substituents in the cyclopentadienyl ligands on the stereoselectivity of these reactions.

References

1 F. Turecek, H. Antropiusova, K. Mach, V. Hanus and P. Sedmera, Tetrahedron Lett., (1980) 637.
2 K. Mach, F. Turecek, H. Antropiusova, L. Petrusova and V. Hanus, Synthesis, (1982) 53.
3 H. Akita, H. Yasuda, K. Nagasuma and A. Nakamura, Bull. Chem. Soc. Japan, 56 (1983) 554.
4 K. Mach, H. Antropiusova, V. Hanus and F. Turecek, J. Organomet. Chem., 269 (1984) 39.
5 K. Mach, H. Antropiusova and V. Hanus, Trans. Met. Chem., 10 (1985) 302.
6 E. Samuel, J. Organomet. Chem., 198 (1980) C65.
7 H.G. Alt and M.D. Rausch, J. Amer. Chem. Soc., 96 (1974) 5936.
8 M. Peng and C.H. Brubaker, Inorg. Chim. Acta, 26 (1978) 231.
9 M.D. Rausch, W.H. Boon and H.G. Alt, J. Organomet. Chem., 141 (1977) 299.
10 E. Samuel, P. Maillard and C. Giannotti, J. Organomet. Chem. 142 (1977) 299.
11 P.W.N.M. van Leeuwen, H. van der Heijden, C.F. Rooreck and J.H.G. Frijns, J. Organomet. Chem., 209 (1981) 169.
12 H. Hudson, M.F. Lappert and R. Pichon, J. Chem. Soc., Chem. Commun., (1983) 374.
13 P. Courtot, R. Pichon, Y. Raoult and J.Y. Salaün, to be published.
14 H.A. Martin and F. Jellinek, J. Organomet. Chem., 8 (1967) 115.
15 H.A. Martin and F. Jellinek, J. Organomet. Chem., 12 (1968) 149.
16 H.H. Brintzinger, J. Amer. Chem. Soc., 89 (1967) 6871.