RAPID ISOMERIZATION OF ALLYLIC ALCOHOLS WITH IRIDIUM(I) AND RHODIUM(I) COMPLEXES AT AMBIENT TEMPERATURE

Chong Shik CHIN, Jeonghan PARK, Choongil KIM, Sun Yeoul LEE,
Jun Ho SHIN and Joong Bae KIM

Department of Chemistry, Sogang University, CPO Box 1142, Seoul 121, Korea

Received 28 March 1988; accepted 6 June 1988

Among allylic alcohols, but-3-en-2-ol is most rapidly isomerized to give butan-2-one in the presence of $Ir(ClO_4)(CO)(PPh_3)_2$ while 2-methylprop-2-en-1-ol most rapidly undergoes the isomerization to give 2-methylpropanal in the presence of $Rh(ClO_4)(CO)(PPh_3)_2$ at room temperature under hydrogen.

Only a few catalytic systems are known to be active for the isomerization of allylic alcohols to the corresponding carbonyl compounds at room temperature [1,2], although search for the effective catalysts for the isomerization has been carried out for some years [1–11]. During the investigation for the catalytic reactions of unsaturated alcohols, we found a striking difference between the catalytic activities of $Ir(ClO_4)(CO)(PPh_3)_2$ ($\underline{1}$) and $Rh(ClO_4)(CO)(PPh_3)_2$ ($\underline{2}$) for the isomerization of allylic alcohols.

Among allylic alcohols, but-3-en-2-ol ($\underline{3}$) is most rapidly isomerized in the presence of $\underline{1}$ whereas 2-methylprop-2-en-1-ol ($\underline{4}$) most rapidly undergoes the isomerization in the presence of $\underline{2}$ at room temperature under hydrogen (see table 1). This observation prompted us to look into the reaction pathways of the isomerization. The isomerization seems to occur according to eqs. (1) and (2) since (i) complex $\underline{1}$ and $\underline{2}$ are known to react immediately with H_2 to produce $M(H)_2(ClO_4)(CO)(PPh_3)_2$ (M = Ir, Rh) [12], (ii) the isomerization is faster under hydrogen than under nitrogen, and (iii) an intermediate, 2-methylprop-1-en-1-ol [13] was actually detected during the isomerization of $\underline{4}$ in the presence of $\underline{2}$ [14]. Then, the rate data with $\underline{1}$ and $\underline{2}$ in table 1 are explained as follows.

The dihydridoiridium complex, $Ir(H)_2(ClO_4)(CO)(PPh_3)_2$ ($\underline{5}$) is very stable both in solution and in the solid state while the rhodium analogue, $Rh(H)_2(ClO_4)(CO)(PPh_3)_2$ ($\underline{6}$) is much less stable (complex $\underline{6}$ has never been isolated). Accordingly, the second step (k_2 and k_2') would be more facile with the iridium complex than with the rhodium complex, and the first step (k_1 and k_1') might be the rate determining step for the isomerization with $\underline{5}$. Then, the faster isomerization of $\underline{3}$ than that of $\underline{4}$ in the presence of $\underline{1}$ is readily understood by a steric reason, the relative ease of the formation of $\underline{7}$ and $\underline{8}$.

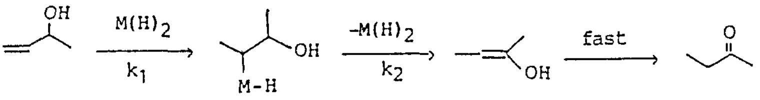
Table 1

Isomerization of allylic alcohols (6.0 mmole) with $Ir(ClO_4)(CO)(PPh_3)_2$ (1) (0.2 mmole) and $Rh(ClO_4)(CO)(PP_3)_2$ (2) 0.2 mmole) in $CDCl_3$ (5.0 ml) at 30 °C under hydrogen (P_{H_2} + vapor pressure of the solution = 1 atm).[1]

catalyst	substrate	product (%)	time (hr)
1	$CH_2{=}CHCH(OH)CH_3$	$CH_3CH_2COCH_3$ (100)	0.5
	$CH_2{=}C(CH_3)CH_2OH$	$(CH_3)_2CHCHO$ (100)	7.0
2	$CH_2{=}CHCH(OH)CH_3$	$CH_3CH_2COCH_3$ (88) $CH_3CH_2CH(OH)CH_3$ (12)	20.0
	$CH_2{=}C(CH_3)CH_2OH$	$(CH_3)_2CHCHO$ (100)	0.5

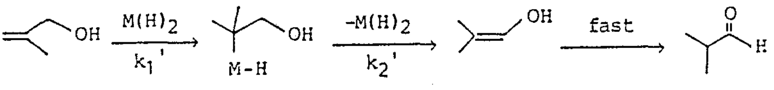
[1] Catalysts were added into the hydrogen-saturated allylic alcohols in $CDCl_3$ in a 25 ml round bottom flask under hydrogen, and the resulting solution was stirred. A part of the reaction mixture (ca. 0.5 ml) was transferred into an NMR tube under hydrogen and analyzed by ^1H NMR measurements at intervals until all of the reactants disappeared.

On the other hand, the second step (k_2 and k_2') could be the rate determining step for the isomerization with 6 since the second step would not be so facile due to the low formation constant of 6. Now the faster isomerization of 4 than that of 3 in the presence of 2 is readily understood since (i) the rhodium complex with tertiary alkyl group (8) would be more reactive than the one with secondary alkyl group (7) and (ii) the rhodium in 8 has two β-hydrogens to produce 6 while there is only one β-hydrogen for the rhodium in 7 to produce 5.



3 7

(1)



4 8

(2)

$M(H)_2 : M(H)_2(ClO_4)(CO)(PPh_3)_2$ (M = Ir, Rh)

Finally, it may be mentioned that the isomerization of allylic alcohols with $[Ir(CO)(PPh_3)_3]ClO_4$ (9) is much slower than that with 1 whereas the isomerization with $[Rh(CO)(PPh_3)_3]ClO_4$ (10) is comparable to that with 2. This observation is understood by the fact that the dissociation of PPh_3 from 10 to give 2 is significant in the solution in the absence of excess PPh_3 while the dissociation of PPh_3 from 9 is negligible.

Acknowledgement

The authors wish to thank the Korea Science and Engineering Foundation and the Ministry of Education, Republic of Korea for the financial support.

References

[1] D. Baudry, M. Ephritikhine and H. Felkin, Nouv. J. Chim. 2 (1978) 355.
[2] H. Alper and K. Hachem, J. Org. Chem. 45 (198) 2269.
[3] G.E. Emerson and R. Pettit, J. Am. Chem. Soc. 84 (1962) 4591.
[4] R. Dramico and T.J. Logan, J. Org. Chem. 32 (1967) 2365.
[5] J.U. Strauss and D.W. Ford, Tetrahedron Lett. (1975) 2917.
[6] Y. Sasson, A. Zoran and J. Blum, J. Mol. Catal. 6 (1979) 289.
[7] Y. Lin and X. Lu, J. Organomet. Chem. 251 (1983) 321.
[8] T. Tasumi, K. Hashimoto, H. Tominaga, Y. Mizuta, K. Hata, M. Hidai and Y. Uchida, J. Organomet. 252 (1983) 105.
[9] J.V.N.V. Prasad and C.N. Pillai, J. Catal. 88 (1984) 418.
[10] A.V. Mushegyan, V.Kh. Ksipteridis, A.O. Gukasyan, O.A. Kamalyan and G.G. Grigoryan, Kinet. Katal. 25 (1984) 81.
[11] K. Felfoldi and M. Bartok, J. Organomet. Chem. 297 (1985) C37.
[12] L. Vaska and J. Peone, Jr., Suom. Kemistil. B44 (1971) 37.
[13] J. Park and C.S. Chin, J. Chem. Soc. Chem. Commun. (1987) 1213.
[14] C.S. Chin, J. Park, S.Y. Lee and C. Kim, J. Organomet. Chem., in press.