Pergamon

Tetrahedron Letters, Vol. 37, No. 7, pp. 1025-1026, 1996

0040-4039/96 $15.00 + 0.00

S0040-4039(96)00039-1

Osmium-Catalysed Cyclopropanation of Olefins

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Abstract. Olefins react with ethyl diazoacetate in the presence of a catalytic amount of $[OsCl_2(p\text{-cymene})]_2$ to produce the corresponding cyclopropanes in good yields (up to 85 %).

Although the transition metal-catalysed reactions of diazo compounds have developed rapidly over the last two decades,[1] work in this area involving osmium complexes has received less attention.[2-5] We recently started studies in this field and, subsequent to our initial report on the use of $OsCl_2(PPh_3)_3$[6] as catalyst for olefin cyclopropanation, we turned our attention to $[OsCl_2(p\text{-cymene})]_2$[7] (*p*-cymene = 4-isopropyltoluene). This complex is isoelectronic to $[RuCl_2(p\text{-cymene})]_2$ which is an excellent catalyst precursor for both olefin cyclopropanation and olefin metathesis.[8] We present here our preliminary results on the use of $[OsCl_2(p\text{-cymene})]_2$ as catalyst for the cyclopropanation of olefins by ethyl diazoacetate (Table 1).

The -unoptimized- results show that the use of $[OsCl_2(p\text{-cymene})]_2$ provided high cyclopropanation yields (up to 85 %) with activated olefins such as styrene and styrene derivatives. Non-activated linear and cyclic olefins were much less reactive. For example, cyclooctene was cyclopropanated in only 25 % yield with

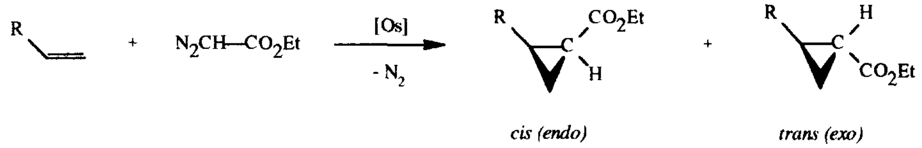

Table 1. Catalytic Cyclopropanation Using $[OsCl_2(p\text{-cymene})]_2$[a]

Olefin	Temperature :	Yield, %[b] (*cis/trans* or *endo/exo* ratio) 60 °C	80 °C
Styrene		59 (0.56)	78 (0.60)
4-Methylstyrene		66 (0.50)	85 (0.65)
4-*t*-Butylstyrene		57 (0.62)	79 (0.67)
4-Methoxystyrene		61 (0.55)	84 (0.62)
4-Chlorostyrene		57 (0.55)	75 (0.51)
α-Methylstyrene		62 (1.5)	79 (1.45)
1-Hexene		1	-
1-Octene		-	8 (0.55)
Cyclohexene		-	14 (0.65)
Cyclooctene		13 (1.45)	26 (1.18)

[a] Reaction conditions : olefin, 20 mmol; $[OsCl_2(p\text{-cymene})]_2$, 0.005 mmol; ethyl diazoacetate, 1 mmol, diluted in 1 mL of the olefin; perfusion time, 4 h; temperature, 60 or 80 °C, except for 1-hexene, 50 °C.

[b] Yield based on ethyl diazoacetate and determined by GC, by comparison with authentic samples. Diethyl maleate and diethyl fumarate represented the major (85-95 %) by-products. Some polystyrenes were also obtained, as well as some metathesis products (ethylene, *trans*-stilbene, and poly(1-octenylene)) from 80 °C (with styrene, ± 5 turnovers at 80 °C, 80 turnovers at 100 °C; with cyclooctene, 3 % ROMP (ring-opening metathesis polymerisation) at 80 °C).

ethyl diazoacetate and practically no olefin metathesis was observed (3 %). By contrast, under the same reaction conditions, the ruthenium analogue [$RuCl_2$(*p*-cymene)]$_2$ was shown to be slightly less efficient for the cyclopropanation reaction but more efficient for olefin metathesis.[8] In competitive cyclopropanation reactions with ethyl diazoacetate, performed at 80 °C in the presence of [$OsCl_2$(*p*-cymene)]$_2$, styrene has been shown to be 15 times more reactive than cyclooctene[9] and 40 times more reactive than 1-octene. Additionally, raising the reaction temperature caused a dramatic increase both in the decomposition rate of the diazo compound (Figure 1) and the cyclopropanation yield (Figure 2).

In most cases, the stereoselectivities (*cis/trans* or *endo/exo* ratios) compare with those reported for typical rhodium- and ruthenium-based catalytic systems : the *trans* (*exo*) isomer is favored. With α-methylstyrene and cyclooctene, however, the *cis/trans* and *endo/exo* ratios are usually high (> 1).

In conclusion, [$OsCl_2$(*p*-cymene)]$_2$ is so far the most selective catalyst for the cyclopropanation of activated olefins. Such a high selectivity is of utmost importance as far as fine organic synthesis is concerned. Studies are under way in our laboratory to extend the reaction to a wider variety of olefins.

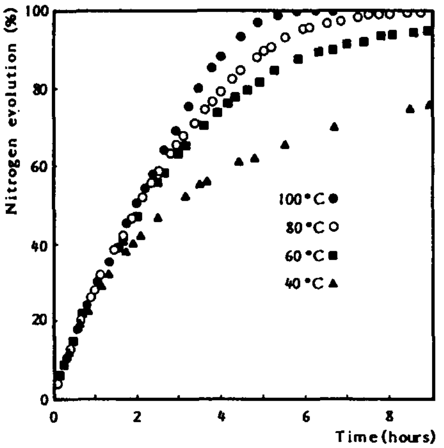

Figure 1. Nitrogen evolution *versus* time for addition of ethyl diazoacetate to styrene.

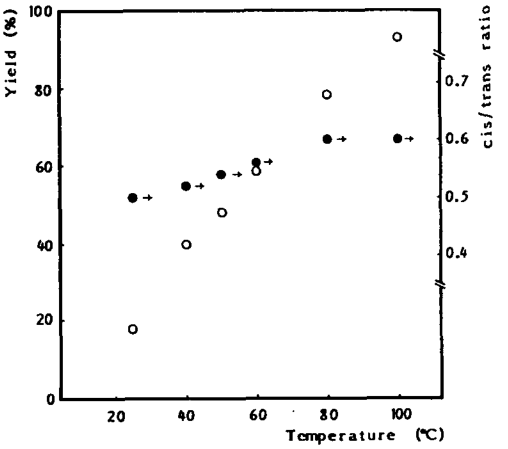

Figure 2. Cyclopropanation yield and *cis/trans* ratio *versus* temperature for addition of ethyl diazoacetate to styrene.

(Reaction conditions : [$OsCl_2$(*p*-cymene)]$_2$, 0.005 mmol; styrene, 2.5 mL; ethyl diazoacetate, 1 mmol, diluted in 1 mL of styrene; perfusion time, 4 h).

Acknowledgements. We thank INTAS (contract n° 94-541) and the National Fund for Scientific Research (F.N.R.S.), Belgium, for the purchase of major instrumentation.

REFERENCES AND NOTES

1. (a) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75-253. (b) Ye, T.; McKervey, M.A. *Chem. Rev.* **1994**, *94*, 1091-1160. (c) Noels, A.F.; Demonceau, A. In *Applied Homogeneous Catalysis by Organometallic Complexes*; Cornils, B.; Herrmann, W.A., Eds; Verlag Chemie, *under press*.
2. Tamblyn, W.H.; Hoffmann, S.R.; Doyle, M.P. *J. Organomet. Chem.* **1981**, *216*, C64-C68.
3. Smith, D.A.; Reynolds, D.N.; Woo, L.K. *J. Am. Chem. Soc.* **1993**, *115*, 2511-2513.
4. (a) Woo, L.K.; Smith, D.A. *Organometallics* **1992**, *11*, 2344-2346. (b) Djukic, J.-P.; Smith, D.A.; Young, V.G., Jr.; Woo, L.K. *Ibid.* **1994**, *13*, 3020-3026.
5. Djukic, J.-P.; Young, V.G., Jr.; Woo, L.K. *Organometallics* **1994**, *13*, 3995-4003.
6. Demonceau, A.; Lemoine, C.A.; Noels, A.F.; Chizhevsky, I.T.; Sorokin, P.V. *Tetrahedron Lett.* **1995**, *36*, 8419-8422.
7. (a) Arthur, T.; Stephenson, T.A. *J. Organomet. Chem.* **1981**, *208*, 369-387. (b) Cabeza, J.A.; Maitlis, P.M. *J. Chem. Soc., Dalton Trans.* **1985**, 573-578.
8. (a) Demonceau, A.; Noels, A.F.; Saive, E.; Hubert, A.J. *J. Mol. Catal.* **1992**, *76*, 123-132. (b) Noels, A.F.; Demonceau, A.; Saive, E. In *Advances in Catalyst Design*, Vol. 2, Graziani, M.; Rao, C.N.R., Eds; World Scientific : Singapore-New Jersey-London-Hong Kong, 1992; pp. 73-94. (c) Stumpf, A.W.; Saive, E.; Demonceau, A.; Noels, A.F. *J. Chem. Soc., Chem. Commun.* **1995**, 1127-1128.
9. Under the same reaction conditions, with $Rh_2(OAc)_4$, styrene:cyclooctene = 2.1, *cis:trans* = 0.57, *endo:exo* = 0.50.

(*Received in France* 22 *November* 1995; *accepted* 2 *January* 1996)