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Osmium-Catalysed Cyclopropanation of Olefins

A. Demonceau,* C.A. Lemoine, and A.F. Noels

Laboratory of Macromolecular Chemistry and Organic Catalysis, C.E.R.M.
University of Liège, Sart-Tilman (B.6), B-4000 Liège, Belgium

Abstract. Olefins react with ethyl diazoacetate in the presence of a catalytic amount of $[\text{OsCl}_2(p\text{-cymene})]_2$ 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 $\text{OsCl}_2(\text{PPh}_3)_3$ ⁶ as catalyst for olefin cyclopropanation, we turned our attention to $[\text{OsCl}_2(p\text{-cymene})]_2$ ⁷ (*p*-cymene = 4-isopropyltoluene). This complex is isoelectronic to $[\text{RuCl}_2(p\text{-cymene})]_2$ which is an excellent catalyst precursor for both olefin cyclopropanation and olefin metathesis.⁸ We present here our preliminary results on the use of $[\text{OsCl}_2(p\text{-cymene})]_2$ as catalyst for the cyclopropanation of olefins by ethyl diazoacetate (Table 1).

The -unoptimized- results show that the use of $[\text{OsCl}_2(p\text{-cymene})]_2$ 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

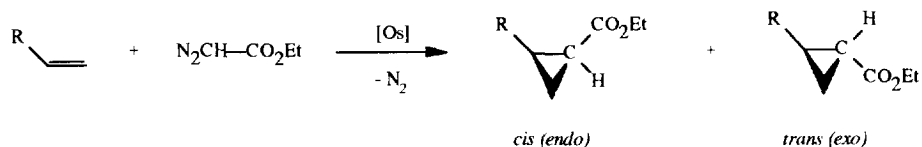


Table 1. Catalytic Cyclopropanation Using $[\text{OsCl}_2(p\text{-cymene})]_2$ ^a

Olefin	Temperature :	Yield, % ^b (<i>cis/trans</i> or <i>endo/exo</i> ratio)	
		60 °C	80 °C
Styrene		59 (0.56)	78 (0.60)
4-Methylstyrene		66 (0.50)	85 (0.65)
4- <i>t</i> -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; $[\text{OsCl}_2(p\text{-cymene})]_2$, 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, \pm 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 $[\text{RuCl}_2(p\text{-cymene})]_2$ 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 $[\text{OsCl}_2(p\text{-cymene})]_2$, styrene has been shown to be 15 times more reactive than cyclooctene⁹ 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, $[\text{OsCl}_2(p\text{-cymene})]_2$ 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.

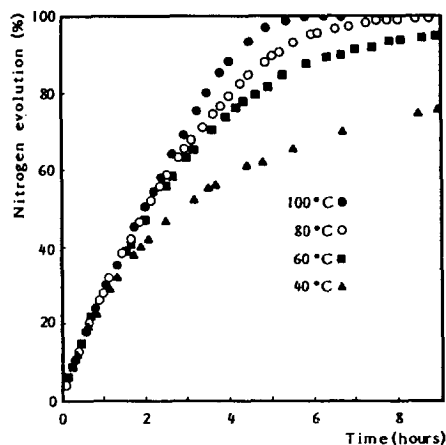


Figure 1. Nitrogen evolution *versus* time for addition of ethyl diazoacetate to styrene.

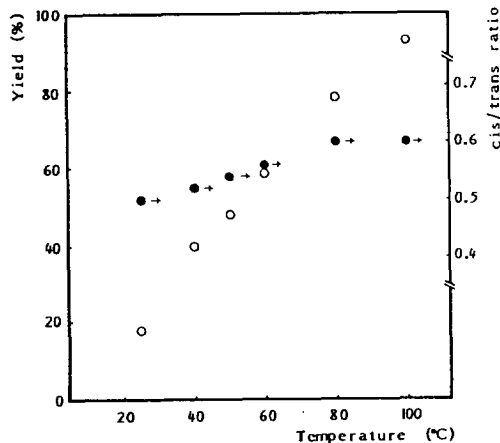


Figure 2. Cyclopropanation yield and *cis/trans* ratio *versus* temperature for addition of ethyl diazoacetate to styrene.

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

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- Under the same reaction conditions, with $\text{Rh}_2(\text{OAc})_4$, styrene:cyclooctene = 2.1, *cis/trans* = 0.57, *endo/exo* = 0.50.