

Shape Selective Alkane Functionalisation by Ethyl Diazoacetate Catalysed by Rhodium Carboxylates

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The unequalled ability of enzymes to exhibit molecular recognition and to catalyse regioselective reactions has led to diverse efforts to design synthetic catalytic systems with similar capabilities. Metalloporphyrins have been used for several years as homogeneous catalysts in a variety of oxidation reactions, including olefin epoxidation and alkane hydroxylation, in attempts to mimic the enzymatic activity of cytochrome P-450. Recently, *very* sterically crowded manganese(III) and iron(III) porphyrin complexes have shown regioselectivities for primary hydroxylation of n-alkanes which are comparable to or even better than those found for some isozymes of cytochrome P-450 [1].



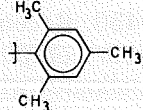


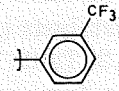
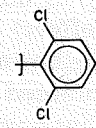
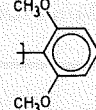
We have already reported the unusual efficiency of rhodium(II) carboxylates for promoting, under mild conditions, the insertion of carbenes into the C-H bonds of alkanes [2]. The aim of this communication is to show that in such reactions, the nature of the catalyst counter-ions largely determines the primary/secondary selectivity of insertion, giving rise to shape selectivity.

In all cases involving unhindered rhodium complexes as catalysts (*e.g.* rhodium acetate, butyrate, benzoate, etc. (entries 2 - 4, 8 and 12, Table 1)), only very modest shape selectivity has proved possible with n-octane (eqn. 1): a relatively large regioselectivity for the insertion into the C₂-H bonds *vs.* internal C₃-H and C₄-H secondary bonds was observed (ω -1 effect). No significant synthesis of primary insertion products took place. Note however that the especially unhindered rhodium formate (entry 1) promoted an unexpected increase in C₁ and C₂ selectivity when compared to higher homologues (entries 2 - 5) and a polycyclic counterpart (rhodium 1-adamantane-carboxylate, entry 7).

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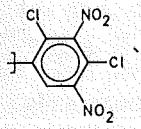

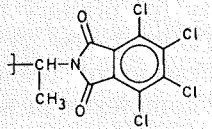
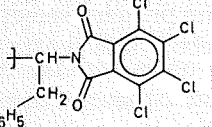
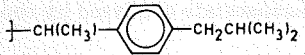
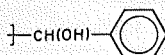
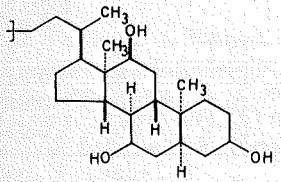
TABLE 1

Selectivity in the homologation of n-octane by ethyl diazoacetate catalysed by various rhodium(II) carboxylates

Catalyst $\text{Rh}_2(\text{O}_2\text{CR})_4$	Products (% yield) ^a				Primary selectivity ^b
	C ₁	C ₂	C ₃	C ₄	
1 R = H	7	57	20	16	0.15
2 CH ₃	3	47	25	25	0.06
3 n-C ₃ H ₇	3	51	24	22	0.06
4 n-C ₆ H ₁₃	2	50.5	25.5	22	0.04
5 n-C ₁₇ H ₃₅	3	50	25	22	0.06
6 CH ₂ Cl	14.5	51	19	15.5	0.34
7 	2.5	49.5	23.5	24.5	0.05
8 	2.5	50.5	24.5	22.5	0.05
9 	3	53	22	22	0.06
10 	10.5	54	19.5	16	0.23 ₅
11 	3.5	49.5	23.5	23.5	0.07
12 	3	54	23	20	0.06
13 	6.5	53	20.5	20	0.14
14 	4	51	24	21	0.08 ₅

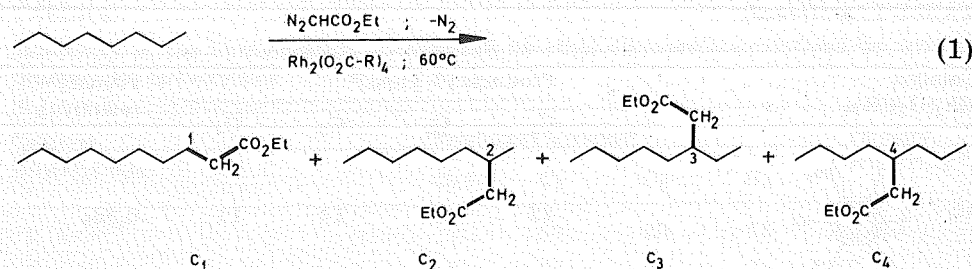
(continued)

TABLE 1 (continued)

Catalyst $\text{Rh}_2(\text{O}_2\text{CR})_4$	Products (% yield) ^a				Primary selectivity ^b
	C ₁	C ₂	C ₃	C ₄	
15 	22	53	14	11	0.56 ₅
16 	0.5	53	25.5	21	0.01
17 	9	53	21	17	0.20
18 	12	55	18	15	0.27
19 	2	48	26	24	0.04
20 	10.5	46.5	22.5	20.5	0.23 ₅
21 	4.5	58.5	21.5	15.5	0.09 ₅
22 9-triptycenylic	19	53	14	14	0.47
23 CF ₃ (22°C)	6	51	23	20	0.13
24 THERMAL (150°C)	24	31	23	22	0.63

^aReaction conditions: n-octane 5 ml (30 mmol); catalyst 5 mg; ethyl diazoacetate 1 mmol diluted to 1 ml by the substrate; addition time 4 h with an automatic syringe; 60 °C.

^bThe ratio of total primary insertion products to total secondary insertion products normalized for the relative number of hydrogen atoms.



In contrast, the more sterically demanding rhodium complexes of 9-triptycencarboxylic acid (entry 22) as well as 2,4-dichloro-3,5-dinitrobenzoic acid (entry 15) promoted good regioselectivity for primary functionalization of n-alkanes (up to 30% yield at C₁, Tables 1 and 2), and remarkable shape selectivity for primary functionalization of branched alkanes (up to 50% yield) [2b]. With modestly hindered complexes, in which the bulky part of the ligand is remote from the carboxylato bridge by one (entry 17 and 18) or three (entry 21) carbon atoms, the primary selectivity decreases steadily, whereas with rhodium ferrocenecarboxylate (entry 16), insertion at C₁-H is practically suppressed (Table 2).

TABLE 2

Selectivity in the homologation of n-alkanes by ethyl diazoacetate catalysed by rhodium carboxylates 1, 6, 15 and 16^a

Substrate	Catalyst entry	Products (% yield)					Primary selectivity
		C ₁	C ₂	C ₃	C ₄	C ₅	
n-hexane	1	14	55	31			0.22
	6	20.5	55.5	24			0.34
	15	31	49	20			0.60
	16	0.2	52	48			0.003
n-decane	1	5	46	17	18	14	0.14
	6	10.5	41	17.5	17	14	0.31
	15	20.5	46.5	12.5	10.5	10	0.69
	16	0.5	43.5	22	18	16	0.013

^aSame remarks as for Table 1.

We have therefore succeeded in generating substantial changes in regioselectivity for the homologation of n-alkanes by ethyl diazoacetate as a function of steric constraint at the rhodium periphery. Nevertheless, steric hindrance is not the sole factor that controls the selectivity. For instance, rhodium chloroacetate (entry 6) whose bulkiness lies between those of rhodium acetate (entry 2) and rhodium butyrate (entry 3), unexpectedly

also enhances attack on primary C-H bonds*. The homologation of n-octane is similarly, but to a lesser extent, influenced by rhodium 2,6-dichlorobenzoate (entry 13) compared to rhodium 2,4,6-trimethylbenzoate (entry 9). Moreover, rhodium salicylate (entry 10) is more selective for primary insertion than its methyl (entry 9) or trifluoromethyl (entry 11) analogues and, consistent with this, rhodium mandelate (entry 20), although less effective, is also more selective than complex 19. This may be due either to high local polarity in the vicinity of the catalytic centre or to electronic effects generated by the hydroxyl group, since the 2,6-dimethoxy-substituted complex (entry 14) shows no increase in primary selectivity. Our observations prompt therefore the suggestion that a suitably positioned polar group may be able to participate in secondary bonding during alkane functionalization [4].

The possibility remains that with completely unhindered complexes, such as rhodium(II) formate or with complexes bearing a sigma donor group (Cl, OH) suitably positioned on the rhodium-rhodium frame (e.g. entries 6, 15, 20), strong self-association of the complexes might be determinant in poorly coordinating solvents. Evidence for such associations has been reported for rhodium acetate in the solid state [5] and also recently suggested for rhodium perfluorobutyrate in dichloromethane [6]. The existence of the catalyst as an oligomer (cluster-like) in solution would also result in restricted access to the active centre with, as consequence, an increase in the apparent shape selectivity effects.

Acknowledgements

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*This is in agreement with the large increase in the homologation of the methyl group of n-alkanes using diazoesters and a chloro-substituted tetraphenylporphyrin complex of rhodium(III), as compared to the methyl and unsubstituted ones [3].