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SYNTHESIS OF METHYL KETONES BY RHODIUM AND RUTHENIUM CATALYZED OXIDATION REACTIONS UNDER PHASE TRANSFER CONDITIONS

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Abstract: *The use of rhodium and ruthenium complexes as catalysts for the phase transfer catalyzed oxidation of olefins is described, and compared with the palladium catalyzed Wacker reaction.*

Much work has been done on the palladium catalyzed oxidation of olefins to ketones (Wacker-type reaction).[1] In the preceding communication[2], we reported that phase transfer catalysis enables one to effect oxidation under mild conditions, with the structure of the quaternary ammonium salt critical to the success of the reaction. This communication describes the use of ruthenium and rhodium compounds as catalysts for the oxidation of olefins to ketones.

Exposure of 1-decene to oxygen, water, benzene, hydrated rhodium chloride as the metal catalyst, cupric chloride as the re-oxidant, and cetyltrimethylammonium bromide (CTAB) as the phase transfer agent afforded 2-decanone in 44% yield. (The procedure was identical to that using palladium chloride, except for the change in metal catalysts.)[2] This transformation could also be achieved with the dimer of 1,5-hexadienerhodium chloride [(1,5 HDRhCl)$_2$], a rhodium(I) compound[3]. Several ruthenium compounds could also be used, including dichlorotris(triphenylphosphine)ruthenium(II) and ruthenium(III) chloride, while tris(acetylacetonato)ruthenium(III) and [Ru(CO)$_3$Cl$_2$]$_2$ were ineffective for the oxidation reaction.

There are several interesting differences between the rhodium and ruthenium catalyzed oxidation reactions, when compared with the use of palladium chloride as the catalyst. First, the rhodium and ruthenium catalyzed reactions occur using small or large quaternary ammonium ions, while only large lipophilic phase transfer catalysts permit the palladium catalyzed Wacker reaction to take place. Specifically, tetrabutylammonium hydrogen sulfate (THS), which is inactive for the palladium catalyzed reaction is of some use as a phase transfer catalyst for the rhodium or ruthenium catalyzed reactions. Second isomerization usually occurs with THS (it also takes place without it) and to a lesser extent, with CTAB, using rhodium(I) as the catalyst-isomerization products were, with one exception, not formed with palladium. Third, the palladium(II) catalyzed reaction of dienes such as 1,7-octadiene or 1,9-decadiene is selective, affording only diketones. However, in the case of rhodium, the reaction is not selective, giving mixtures of diketones, monoketones, and isomerized dienes.

In 1978, Mimoun and co-workers[4] reported the homogeneous oxidation of olefins to ketones using rhodium complexes, including hydrated rhodium(III) chloride, as the catalyst. This is not a Wacker-type reaction since water inhibits the reaction, and co-catalysts such as cupric chloride are not necessary (i.e., copper does not participate in the oxidation). The phase transfer catalyzed oxidation reaction, in contrast, appears to be a genuine Wacker process since it is not inhibited by water, and a co-catalyst [$CuCl_2 \cdot H_2O$], is required.

TABLE 1

RHODIUM AND RUTHENIUM PHASE TRANSFER CATALYZED OXIDATION OF OLEFINS

Substrate	Metal Catalyst	$R_4N^+X^-$	Products, % Yield
1-Decene	$RhCl_3 \cdot 3H_2O$	CTAB	2-Decanone, 44
	$[1,5\text{-}HDRhCl]_2$	CTAB	2-Decanone, 34
	$[1,5\text{-}HDRhCl]_2$	THS	2-Decanone, 40. Internal decenes, 44.
	$[1,5\text{-}HDRhCl]_2$	-	Internal decenes, 35
	$Rh_2(OAc)_4$	THS	2-Decanone, 21
	$RuCl_2(PPh_3)_3$	CTAB	2-Decanone, 64
	$RuCl_2(PPh_3)_3$	THS	2-Decanone, 28
	$RuCl_3$	CTAB	2-Decanone, 13. 2-Decene, 5.
1-Dodecene	$RhCl_3 \cdot 3H_2O$	CTAB	2-Dodecanone, 35
	$[1,5\text{-}HDRhCl]_2$	THS	2-Dodecanone, 25. Internal dodecenes, 56.
1,7-Octadiene	$[1,5\text{-}HDRhCl]_2$	THS	2,7-Octanedione, 5. Octenones, 27[a] Diene isomers, 67
1,9-Decadiene	$RhCl_3 \cdot 3H_2O$	CTAB	2,9-Decanedione, 8. 9-Decen-2-one, 33
	$[1,5\text{-}HDRhCl]_2$	CTAB	2,9-Decanedione, 9. Decenones, 28 Diene isomers, 43
	$[1,5\text{-}HDRhCl]_2$	THS	2,9-Decanedione, 6. Deceneones, 23[b] Diene isomers, 67

[a] 2:1 ratio of 7-octene-2-one: internal octenones. [b] 3:1 ratio of 9-decene-2-one: internal decenones.

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