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PALLADIUM AND PHASE TRANSFER CATALYZED OXIDATION OF OLEFINS TO KETONES. SENSITIVITY OF THE REACTION TO THE NATURE OF THE PHASE TRANSFER AGENT.

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Summary: Terminal olefins can be converted to ketones in good yields, and under mild conditions, using phase transfer catalysis; the quaternary ammonium salt governs the course of the reaction.

Many applications of phase transfer catalysis in organic chemistry have been described in the literature during the past eighteen years[1-3]. The use of such biphasic media for effecting reactions catalyzed by metal complexes is a more recent development.[4-6] Advantages of such processes over conventional methods include significant enhancement in reaction rates, and simplicity both in execution and workup of the reaction.

There have been no publications, to our knowledge, on metal complex catalyzed oxidation reactions of olefins to ketones under phase transfer conditions. Recently, we initiated an investigation of several industrially important oxidation processes[7], and now wish to report that the conversion of olefins to ketones (Wacker chemistry) can be achieved under mild conditions by phase transfer techniques. Furthermore, the nature of the quaternary ammonium salt used as the phase transfer catalyst has a very significant influence on the reaction.

When oxygen was bubbled, at 80°C, through a benzene solution of 1-decene, water, palladium chloride, cupric chloride, and cetyltrimethylammonium bromide (CTAB) as the phase transfer agent, pure 2-decanone was obtained in 73% yield, together with 2% of 2-decene. The ratio of olefin to palladium chloride was 25:1, with lower product yields (40-50%) realized by the use

$$RCH{=}CH_2 + O_2 \xrightarrow[R_4N^+X^-,C_6H_6,H_2O,80°,1\ atm.]{PdCl_2,CuCl_2{\cdot}2H_2O} RCOCH_3$$

of lower or higher ratios [e.g., 50/1 ratio of 1-decene/$PdCl_2$ gave 2-decanone in 48% yield, and 42% of internal decenes]. Good yields of monoketones were also obtained when other 1-olefins [e.g., 1-butene] were employed as reactants while terminal dienes such as 1,7-octadiene and 1,9-decadiene gave diketones with no detectable quantities of unsaturated monoketones as by-products. The yields of analytically pure products are given in Table 1. No reaction occurs in the absence of CTAB. Modest conversions [up to 35% 2-decanone] result when a limited amount of water [0.5 ml.] is used as the aqueous phase, and CTAB is the phase transfer catalyst. Palladium(0) catalysts can also be used in these reactions, the most effective being bis(dibenzylideneacetone)palladium(0) [55% yield of 2-decanone].

Table 1

PHASE TRANSFER CATALYZED OXIDATION OF OLEFINS AT ATMOSPHERIC PRESSURE

Substrate	$R_4N^+X^-$[a]	Products,% yield[b]
1-decene	CTAB	2-decanone, 73
		2-decene, 2
	$n\text{-}C_{14}H_{29}N(CH_3)_3{}^+Br^-$	2-decanone, 54
	DTAC	2-decanone, 54
	$n\text{-}C_{12}H_{25}N(CH_3)_2C_2H_5{}^+Br^-$	2-decanone, 33[c]
	Aliquat 336	2-decanone, 9
	$PhCH_2N(C_2H_5)_3{}^+Cl^-$	-
	$(C_4H_9)_4N^+HSO_4{}^-$	-
1-dodecene	CTAB	2-dodecanone, 62
	$(C_4H_9)_4N^+HSO_4{}^-$	-
	$PhCH_2N(C_2H_5)_3{}^+Cl^-$	-
1-pentene	CTAB	2-pentanone, 48[d]
1-butene	CTAB	2-butanone, 65[e]
vinylcyclohexane	CTAB	methylcyclohexyl ketone, 22
1,7-octadiene	CTAB	2,7-octanedione, 77
1,9-decadiene	DTAC	2,9-decanedione, 78
	$(C_4H_9)_4N^+HSO_4{}^-$	-

[a] CTAB = cetyltriethylammonium bromide; DTAC = dodecyltrimethylammonium chloride. [b] Yields are ofpure materials. The remainder is unreacted starting material. [c] Yield was 31% using hexane as the organic phase with 69% recovered 1-decene. [d] 45 psi. [e] 180 psi.

Two noteworthy features of the reaction are that the metal catalyst can be re-used after reaction with only a slight reduction (< 5%) in yield, and that air can be used instead of oxygen. Allylic alcohols were not formed in any of these reactions. Internal olefins [e.g., cis or trans-2-decene] are inert under the reaction conditions, as are 1,1-disubstituted alkenes [2-methyl-1-undecene]. Internal olefins are formed (no oxidation) when terminal olefins are exposed to oxygen, $PdCl_2$, water and benzene [i.e., without cupric chloride or a quaternary ammonium salt].

A novel aspect of the oxidation process is its dependence on the type of phase transfer agent. Olefins are oxidized only by the use of large lipophilic phase transfer catalysts. These include CTAB, tetradecyltrimethylammonium bromide and dodecyltrimethylammonium chloride (DTAC)(Table 1). In the latter case, change of one methyl group to ethyl (and chloride to bromide) results in lower product yields and in the recovery of more substrate. With quaternary ammonium salts containing alkyl groups of shorter chain length than twelve carbons, little or no oxidation occurs. These include Aliquat 336 (tricaprylmethylammonium chloride), benzyltriethylammonium chloride, and tetrabutylammonium hydrogen sulfate.

The oxidation reaction does not appear to be of micelle character since attempted oxidation of 1-decene using sodium dodecyl sulfate in place of CTAB gave only a mixture of isomeric decenes[8]. Instead, the relative extractability and solubility, in the organic phase, of ionic species derived from the different quaternary ammonium salts, may govern the course of the reaction[9].

The following procedure is typical: a mixture of $CuCl_2 \cdot 2H_2O$[10 mmol] and $PdCl_2$[1.0 mmol] in water [10 ml.] was stirred for 10 minutes. Then 1-decene [3.51 g., 25 mmol] was added followed by benzene [15 ml.] and cetyltrimethylammonium bromide [2.0 mmol]. Oxygen was bubbled through the solution at 80°C for 48 hours. After cooling to room temperature, ethyl acetate (15 ml.) was added and the solution was filtered. The filtrate was dried ($MgSO_4$), and then distilled affording pure 2-decanone in 73% yield and 2-decene in 2% yield.

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