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ACTIVATION OF POLYHALOALKANES BY PALLADIUM CATALYST. PALLADIUM CATALYZED OXIDATION OF ALCOHOLS TO CARBONYL COMPOUNDS WITH CARBON TETRACHLORIDE

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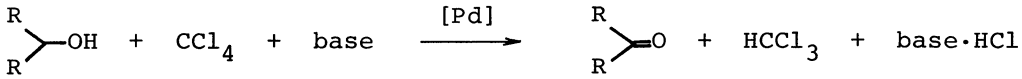
$Pd(OAc)_2$ and $PdCl_2$ are good catalyst for the oxidation of alcohols to carbonyl compounds with CCl_4 in the presence of bases. Primary and secondary alcohols are oxidized to esters and ketones in high yields, respectively.

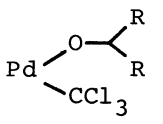
In a previous paper, we have reported the palladium catalyzed addition reaction of CCl_4 to olefins.[1] In our further studies on the palladium catalyzed activation of polyhaloalkanes, we found that alcohols can be oxidized to carbonyl compounds with CCl_4 by using a palladium catalyst.

The oxidation was carried out in the presence of bases such as K_2CO_3 with a catalytic amount of $PdCl_2$ or $Pd(OAc)_2$ by heating a mixture of alcohol and CCl_4 (ca. 5 equiv.). As shown in the table, primary alcohols are oxidized to the corresponding esters, and secondary alcohols are oxidized cleanly to ketones. Benzyl alcohol is somewhat exceptional and affords a mixture of benzaldehyde, benzyl benzoate, and dibenzyl ether. It was confirmed by G.L.C. analysis that equimolar amounts of acetone and chloroform were formed by the reaction of 2-propanol with CCl_4. Thus, the overall reaction of secondary alcohols can be expressed by the following equation.

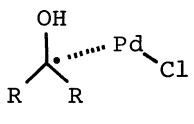


In a typical example, to a mixture of $PdCl_2$ (2 mg, 0.01 mmol) and K_2CO_3 (138 mg, 1 mmol) was added 2-octanol (130 mg, 1 mmol) dissolved in CCl_4 (1 mL), and the suspension was gently refluxed under argon atmosphere. After 24 h, the mixture was filtered to remove potassium salts and concentrated. Purification by column chromatography (hexane-ether) afforded 2-octanone in 65% yield.

Two mechanisms can be proposed for the reaction. The reaction may proceed through the formation of trichloromethyl-alkoxy-palladium complex $\underset{\sim}{1}$ as one explanation.[2-4] Another is the formation of the free radical intermediate $\underset{\sim}{2}$.[5,6] Although no intermediate was detected, coordination or interaction of CCl_4 and alcohol with palladium seems to play an important role in this reaction.



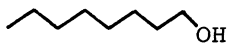
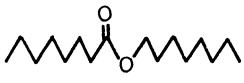
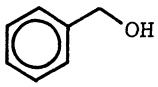
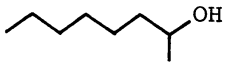
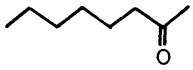
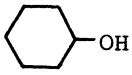
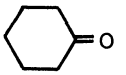
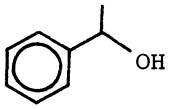
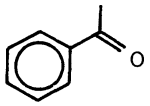
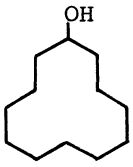
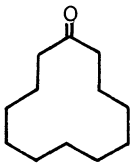
$\underset{\sim}{1}$



$\underset{\sim}{2}$

Further investigation of the palladium catalyzed activation of polyhaloalkanes and the reaction of other functionalized alcohols with CCl_4 is in progress.

Table

	Cat.(%)	Temp(°C)	Time(h)	Product	Yield(%)
	1	80	24		73
	2	80	7	PhCHO (57) $PhCO_2CH_2Ph$ (35) $PhCH_2OCH_2Ph$ (8)	70
	1	80	24		65
	2	80	72		63
	2	80	24		55
	1	120	24		75
	2	80	72		35
	1	120	24		55

References

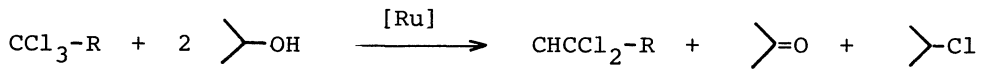
1) J.Tsuji, K.Sato, and H.Nagashima, Chem. Lett., 1981, 1169.

2) A similar intermediate as 1 was suggested by Tamaru et al, for the oxidation of alcohols with halobenzenes in the presence of palladium-phosphine complexes.[3,4]

3) Y.Tamaru, K.Inoue, Y.Yamada, and Z.Yoshida, Tetrahedron Lett., 1981, 1801.

4) Y.Tamaru, Y.Yamamoto, Y.Yamada, and Z.Yoshida, Tetrahedron Lett., 1979, 1401.

5) We found that the oxidation of alcohols with CCl_4 also proceeded using other transition metal catalysts, such as $RuCl_2(PPh_3)_3$, CuCl, $Fe(CO)_5$, and $Mo(CO)_6$, at elevated temperature. It was reported that the Ru complex was a useful catalyst for the reduction of 1,1,1-trichloroalkanes in the presence of 2-propanol to form 1,1-dichloroalkanes as expressed by the following equation.[6]



6) Y.Sasson and G.L.Rempel, Synthesis, 1975, 448.

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