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ACTIVATION OF POLYHALOALKANES BY PALLADIUM CATALYST. FACILE ADDITION OF POLYHALOALKANES TO OLEFINS

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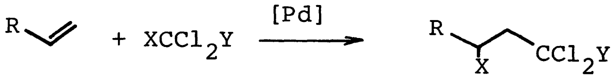
Addition reaction of CCl_4, CCl_3Br, and CCl_3CO_2Me to olefins proceeded under mild conditions to afford 1 : 1 adduct in high yields by using palladium-phosphine complexes as a catalyst in the presence of bases. The reaction proceeded even at room temperature.

It is known that addition reaction of polyhaloalkanes such as CCl_4 to olefins is catalyzed by radical initiators.1) In addition, a number of transition metal salts and complexes such as copper and iron salts,2) and metal carbonyls3,4) also catalyze the reaction. Recently $RuCl_2(PPh_3)_3$ was found to exhibit very high activity.5) However, no report has been given, so far, that palladium complexes are active for the reaction of polyhaloalkanes with olefins, and this is somewhat peculiar in view of the fact that palladium complexes show an excellent catalytic activity for the reaction of alkenyl and aryl halides with olefins to afford styrene and diene derivatives.6) In this paper, we wish to report that palladium-phosphine complexes are active catalysts for the addition reaction of CCl_4, CCl_3Br, and CCl_3CO_2Me to various olefins.

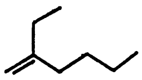
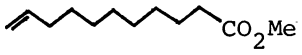
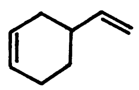


X=Cl, Br Y=Cl, CO_2Me

We investigated the reactions of several terminal olefins with CCl_4, CCl_3Br, and CCl_3CO_2Me by using $Pd(OAc)_2$-PPh_3 as a catalyst. The optimum ratio of Pd : PPh_3 was found to be 1 : 2. The results are summarized in the table. For this reaction it is essential to add an excess of bases such as NaOAc and K_2CO_3. Since $Pd(PPh_3)_4$ is reportedly converted to $PdCl_2(PPh_3)_2$ by the action of CCl_4,7) it is likely that the presence of base is important to keep the palladium species at zerovalent state. Interestingly, we found that the reaction proceeded with high yields when it was carried out under carbon monoxide atmosphere (entry 1). Thus the palladium catalyst is very active and high yields of addition products were obtained even at room temperature. It was confirmed that other catalysts such as $(PhCO_2)_2$, CuCl, and $RuCl_2(PPh_3)_3$ exhibited no catalytic activity when the reaction was carried out at temperatures lower than 40°C, whereas the palladium catalyst showed the high activity (entries 1d - 1f).

Internal olefins also react with CCl_4 and CCl_3Br. The reactions of *cis*- and *trans*-2-butenes gave a mixture of diastereomers in a ratio of 4 : 1. This ratio is the same as obtained by CuCl or $(PhCO_2)_2$ as catalysts.2) In the reaction of cyclohexene, the palladium catalyst afforded a mixture of *cis*- and *trans*-adducts in a similar ratio as radical initiators (45 : 55). These results are different from the results obtained by the Ru complex, which gave a different ratio of the diastereomers (4 : 96).8)

Table[a]

		$XCCl_2Y$(equiv.)	Temp(°C)	Time(h)	Atm.	Yield(%)
1.		a. CCl_4 (5)	100	5	Ar	77
		b.	100	3	Ar	(54)[c]
		c.	80	3	CO	(60)[c]
		d.	40	5	CO	(20)[c]
		e.	r.t.	120	CO	90
		f. CCl_3Br (1)	40	5	Ar	(88)[c]
		g. (2)[d]	100	3.5	Ar	84
		h. CCl_3CO_2Me (5)[d]	100	15	Ar	64
		i.	80	7	CO	62
2.		CCl_4 (5)	110	20	CO	71
3.		CCl_4 (5)	80	5	CO	58
4.		a. CCl_4 (5)	110	22	CO	20
		b. CCl_3Br (1)	80	7	CO	83
5.		CCl_3Br (1)	80	7	CO	54[b]

[a] All reactions were carried out in the presence of $Pd(OAc)_2$-PPh_3 (1 : 2, 1 mol%) and K_2CO_2 (2 equiv.) in benzene or toluene in the atmosphere of argon (Ar) or carbon monoxide (CO).

[b] 3-Bromo-1,1,1-trichloro-(3-cyclohexenyl)-propane was obtained as a sole product.

[c] The yields were determined by G.L.C..

[d] NaOAc was used instead of K_2CO_3.

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