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ACTIVATION OF POLYHALOALKANES BY PALLADIUM CATALYST. PREPARATION OF γ-TRICHLORO ESTERS BY COADDITION REACTION OF CARBON TETRACHLORIDE AND CARBON MONOXIDE TO OLEFINS

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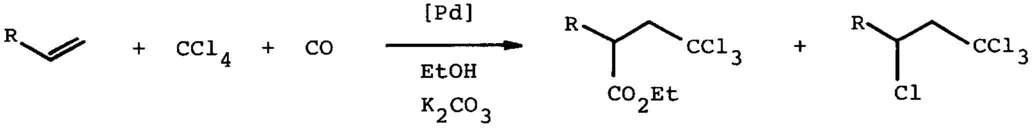
Summary: $Pd(OAc)_2$ combined with PPh_3 catalyzed the coaddition reaction of CCl_4 and CO to olefins in ethanol to afford ethyl 2-alkyl-4,4,4-trichlorobutanoates. The best yields were obtained when the reaction was carried out in the presence of K_2CO_3 at low temperature.

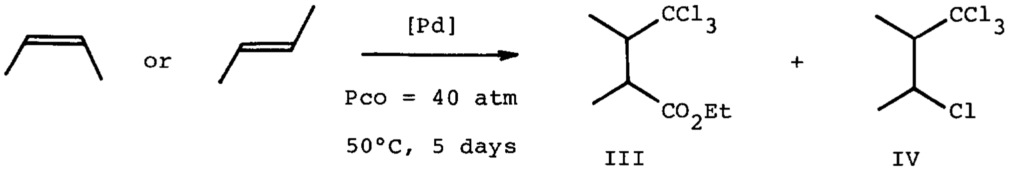
It is well-known that palladium exhibits excellent catalytic activity in carbonylation reaction of various organic halides. For example, halogen atoms of allyl, benzyl, alkenyl, and aryl halides are transformed to esters by the palladium catalyzed carbonylation in alcohols.[1-5] Recently, we found that facile activation of CCl_4 and other polyhaloalkanes with palladium catalyst takes place in the presence of a base to give rise to addition reaction to olefins,[6] oxidation of alcohols,[7] and formation of γ-trichloro ketones from 1-alken-3-ols.[8] Then, we turned our attention to the possibility of the palladium catalyzed reaction of polyhaloalkanes with CO, and found the formation of γ-trichloro esters by coaddition of CCl_4 and CO to olefins in ethanol. In this paper, we wish to report results of this carbonylation reaction.



I II

The reaction of 1-octene with excess CCl_4 under CO pressure (20-40 atm) was first investigated. In the presence of one mol% of $Pd(OAc)_2$ combined with PPh_3 (1 : 2) and one equivalent of K_2CO_3 for the olefin, the reaction proceeded smoothly to form ethyl 2-hexyl-4,4,4-trichlorobutanoate accompanied with 1,1,1,3-tetrachlorononane which is formed by a simple addition of CCl_4 to 1-octene. The ratio of the ester to the simple adduct varied with CO pressure and reaction temperature, and the ratio of the ester increased when the reaction was carried out at lower temperature under higher CO pressure. Since total conversion decreased in parallel with lowering of the reaction temperature, 24-48 h were required to obtain the ester in high yields under 40 atm of CO pressure. The reaction also proceeded in the absence of either K_2CO_3 or PPh_3, but the yield was somewhat lower. Choice of ligand also influenced the yields of the ester; 1,2-bis(diphenylphosphino)ethane and tri-*o*-tolylphosphine were as suitable as PPh_3, whereas Bu_3P and $(PhO)_3P$ gave inferior results. When the reaction was carried out in other alcohols such as methanol and isopropyl alcohol, the corresponding esters were formed, but in lower yields. Interestingly, in the simple addition reaction of polyhaloalkanes by the palladium catalyst, $BrCCl_3$ is far more reactive than CCl_4, while in the carbonylation reaction, only the simple adduct of $BrCCl_3$ was obtained under the same conditions.

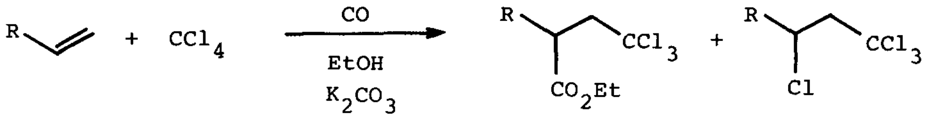
Other olefins also underwent the carbonylation. As shown in the table, the corresponding γ-trichloro esters were obtained from safrole, methyl 10-undecenoate, and ethyl 4-pentenoate in 30-60% yields accompanied with the corresponding simple adducts of CCl_4. The reaction of the internal olefinic bond in 2-butene also proceeded smoothly to afford a diastereomeric mixture of γ-trichloro esters and adducts. Thus, *cis*- and *trans*-2-butenes were converted to the corresponding esters and adducts which were mixtures of diastereomers.



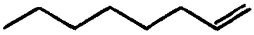
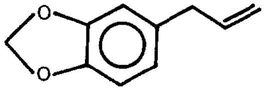
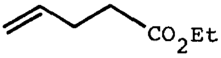
		III	IV
from	*cis*-butene	36%	23%
from	*trans*-butene	33%	28%

In a typical example, a mixture of $Pd(OAc)_2$ (44 mg, 0.2 mmol), PPh_3 (104 mg, 0.4 mmol), K_2CO_3 (2.77 g, 20 mmol) was placed in a stainless steel autoclave (100 mL). 1-Octene (2.24 g, 20 mmol) and CCl_4 (10 mL, ca. 100 mmol) dissolved in ethanol (20 mL) were added, and then CO was introduced (40 atm). The solution was vigorously stirred at 50°C. Efficient stirring was crucial. After 24 h, potassium salts were filtered off, and the filtrate was concentrated. The residue was purified by column chromatography or distillation to afford the desired ester.

Table. Carbonylation of 1-Olefins



I II

Olefin	Temp. (°C)	Pco (atm)	Time (h)	Isolated Yields I	II	I+II	Ratio I/II
	40	40	24	39	20	59	64/34
	50	40	24	50	33	83	60/40
	60	40	24	12	51	63	20/80
	50	20	24	39	59	98	40/60
	50	40	96	22	15	37	59/41
	80	40	48	29	35	64	45/55
	40	40	168	60	16	76	79/21
	r.t.	40	120	37	19	56	66/34
	50	40	48	36	28	64	56/44

It is known that the reaction of CCl_4 in alcohol with olefins in the presence of radical initiators under high CO pressure (higher than 1000 atm) affords the γ-trichloro esters in 10-20% yields.[9] In our previous paper,[10] we have reported that binuclear metal carbonyls such as $Co_2(CO)_8$, $Cp_2Fe_2(CO)_4$, and $Cp_2Mo_2(CO)_6$ also catalyze the reaction under 100-200 atm of CO pressure at an elevated temperature. Compared with these catalysts, the palladium catalyst requires much lower temperature and lower CO pressure to obtain the ester in high yields.

As noted above, various organic halides undergo the palladium-catalyzed carbonylation.[1-5] As one explanation, the coaddition reaction may proceed oxidative addition of CCl_4 onto Pd(0) and subsequent insertion of olefin and CO. However, similar coaddition reaction of other organic halides and CO to olefins is scarecely known in the literature. In fact, it was found that palladium catalyzed reaction of iodobenzene with styrene under CO atmosphere afforded a mixture of stilbene and alkyl benzoate. No coaddition reaction took place. Furthermore, a significant retardation by hydroquinone was observed in the coaddition reaction of CCl_4 and CO to 1-octene, and this result seems to indicate participation of a radical intermediate. Thus, the role of palladium in the coaddition reaction is ambiguous at present. Further investigation should be awaited for elucidation of the mechanism.

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