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PALLADIUM-CATALYZED ADDITION REACTION OF OLEFINS, CARBON TETRACHLORIDE AND CARBON MONOXIDE IN ALCOHOLS TO GIVE 2-ALKYL-4,4,4-TRICHLOROBUTANOATES

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Abstract—Pd(OAc)$_2$ combined with PPh$_3$ is a good catalyst for the addition reaction of CCl$_4$ and CO to olefins in ethanol to afford ethyl 2-alkyl-4,4,4-trichlorobutanoates. The esters were obtained in satisfactory yields when the reaction was carried out at 50° in the presence of K$_2$CO$_3$ under CO pressure.

Palladium salts or complexes are excellent catalysts for carbonylation of organic halides[1] such as allyl,[2–4] benzyl, vinyl, and aryl halides[5–10] under low pressure of CO. The reactions provide useful preparative methods for various types of esters or amides. However, there has been no report on the palladium-catalyzed carbonylation of polyhaloalkanes such as CCl$_4$. Our attempted Pd-catalyzed carbonylation of CCl$_4$ was unsuccessful, indicating that CCl$_4$ is different from other organic halides.

We have previously reported carbonylation of olefins in the presence of CCl$_4$ with bi-nuclear metal carbonyls, such as Co$_2$(CO)$_8$, Cp$_2$Fe$_2$(CO)$_4$ and Cp$_2$Mo$_2$(CO)$_6$, as catalysts.[11] In this reaction, no carbonylation of CCl$_4$ itself to form trichloroacetyl chloride or its derivatives occurs, but incorporation of both CCl$_4$ and CO to olefins takes place to give 4,4,4-trichlorobutanoyl chloride under 100–200 atm of CO pressure at 50–150°. Also Foster *et al.* reported that ethylene, CCl$_4$ and CO in methanol gave trichloro esters [CCl$_3$(CH$_2$CH$_2$)$_n$CO$_2$Me, n = 1,2,3] in 40% conversion under very high pressure (1000 atm) with peroxide as an initiator.[12] We have now tried the Pd-catalyzed reaction of CCl$_4$, CO and olefins. The coaddition reaction proceeded smoothly even at 40–50° under 40 atm of CO pressure in alcohols to give 2-alkyl-4,4,4-trichlorobutanoates. A preliminary report has been published,[13] and details of the coaddition reaction are presented in this paper.

RESULTS AND DISCUSSION

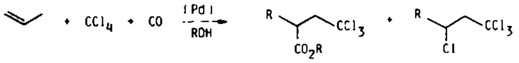
We have reported that Pd(OAc)$_2$ combined with PPh$_3$ catalyzes smooth addition of polyhaloalkanes such as CCl$_4$, BrCCl$_3$ and CCl$_3$CO$_2$Me to olefins in the presence of bases.[14] The reaction is accelerated under CO atmosphere. By increasing CO pressure, we found coaddition reaction of CO and CCl$_4$ to olefins. Results of the reaction of 1-octene under various conditions are summarized in Table 1. Two products, **1** and **2**, were formed by the coaddition reaction and simple addition, respectively, as competitive reactions, and the ratio of these two products changed with reaction conditions.

In this reaction, the presence and choice of bases are important. Although the reaction proceeded in the absence of base, the simple adduct **2** was the main product. Addition of tertiary amines and NaOAc retarded the carbonylation reaction, and the most satisfactory result was obtained with K$_2$CO$_3$, which is insoluble in the reaction medium. Since the reaction medium is heterogeneous, vigorous stirring is important to achieve high yields. Addition of phosphine ligand such as PPh$_3$, tris-(*o*-tolyl)phosphine [P(*o*-Tol)$_3$], and 1,2-bis(diphenylphosphino)ethane (DPPE) improved the yields.

Important factors for achieving high yields of the coadduct are temperature and pressure (entries 1–5). At 90°, no coaddition took place and only the simple adduct **2** was obtained. At room temperature, the reaction was slow. The optimum temperature was around 50°. No coadduct **1** was obtained under atmospheric pressure. By increasing the pressure, the ratio of the coadduct increased.

The reaction was carried out using alcohols as reactants and solvents. Under the same optimum conditions, the yield of the methyl ester was lower in methanol (29%), compared with a 50% yield in ethanol. In isopropyl alcohol, the ester was obtained in 15% yield, and no ester was obtained in t-butyl alcohol (entries 15 and 16). Use of some other solvents gave a rather negative effect. The use of a 1:1 mixture of ethanol and solvents such as DMF, THF and benzene all decreased yields of both products **1** and **2**. Also, attempted synthesis of amides by adding secondary amines instead of alcohols afforded amides in poor yields. For example, in diethylamine, diethylamide and ethylamide were obtained in 7% and 11% yields.

The reactions of other olefinic compounds were carried out under optimum conditions by the use of Pd(OAc)$_2$ combined with PPh$_3$ as the catalyst and



Scheme 1.

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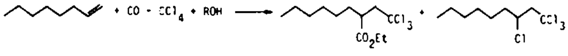
Table 1. Reactions of 1-octene, carbon tetrachloride and carbon monoxide[a]



1 2

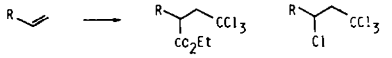
Entry	CO press	Temp	Base	Ligand	ROH	Isolated yield 1	Isolated yield 2
1	20	50	K_2CO_3	PPh_3	EtOH	39	59
2	40	40	K_2CO_3	PPh_3	EtOH	39	20
3	40	50	K_2CO_3	PPh_3	EtOH	50	33
4	40	60	K_2CO_3	PPh_3	EtOH	12	51
5	40	90	K_2CO_3	PPh_3	EtOH	0	35
6	40	50	NaOAc	PPh_3	EtOH	1	16
7	40	50	NEt_3	PPh_3	EtOH	9	8
8	40	50	NBu_3	PPh_3	EtOH	0	0
9	40	50	none	PPh_3	EtOH	22	39
10	40	50	K_2CO_3	P(*o*-Tol)$_3$	EtOH	36	29
11	40	50	K_2CO_3	PBu_3	EtOH	14	10
12	40	50	K_2CO_3	$P(OPh)_3$	EtOH	29	35
13	40	50	K_2CO_3	DPPE	EtOH	40	24
14	40	50	K_2CO_3	none	EtOH	15	10
15	40	50	K_2CO_3	PPh_3	MeOH	29	31
16	40	50	K_2CO_3	PPh_3	i-PrOH	15	19

[a] All reactions were carried out in the presence of $Pd(OAc)_2$ (1 mol%), ligand (2 mol%) and K_2CO_3 (100 mol%) for 24 hr.

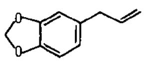
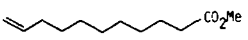
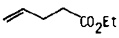
K_2CO_3 as the base in ethanol under 40 atm of CO pressure. Propylene, safrole, methyl 10-undecenoate and ethyl 4-pentenoate were converted to mixtures of the coadducts and simple adducts as shown in Table 2. Formation of polymeric compounds was observed with propylene. Attempted reactions of 1,1-disubstituted olefins, such as isobutylene and 2-ethylhexene afforded only simple adducts. Allyl acetate and cyclohexene afforded mixtures of intractable products.

The reaction of 2-butenes with CCl_4 under CO pressure was not stereospecific, giving a diastereomeric mixture of ethyl 2,3-dimethyl-4,4,4-trichlorobutanoate (**11**). GLC analysis showed the diastereomer ratio to be approximately 4 : 1, when *cis*- or *trans*-2-butene were used. The simple adduct **12** formed simultaneously was also a mixture of diastereomers in a ratio of 4 : 1, which is similar to the ratio obtained in the simple addition reaction under argon atmosphere.[14] The reaction of CCl_4 with CO under similar conditions gives none of the

Table 2. The coaddition reaction of various olefins with CCl_4 and CO[a]

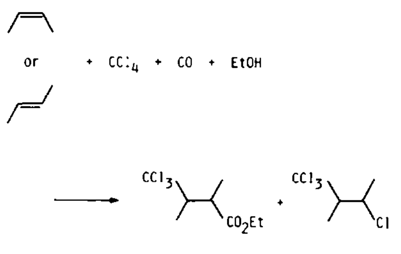


A B

Olefin	Temp (°)	Time (hr)	Isolated yields[b] A	Isolated yields[b] B
	room temp	96	12	25
			(3)	(4)
	50	96	22	15
	80	48	29	35
			(5)	(6)
	40	168	60	16
			(7)	(8)
	room temp	120	37	19
	50	48	36	28
	50	168	43	32
			(9)	(10)

[a] All reactions were carried out in the presence of $Pd(OAc)_2$ (1 mol%), PPh_3 (2 mol%) and K_2CO_3 (100 mol%) in ethanol under CO pressure (40 atm). The yields were determined by isolation.

[b] Numbers in parentheses are compound numbers cited in the experimental section.



	11	**12**
from cis	36%[a]	23%[a]
	(74 : 26)[b]	(77 : 23)[b]
from trans	33%[a]	28%[a]
	(75 : 25)[b]	(78 : 22)[b]

[a]. Isolated yields.

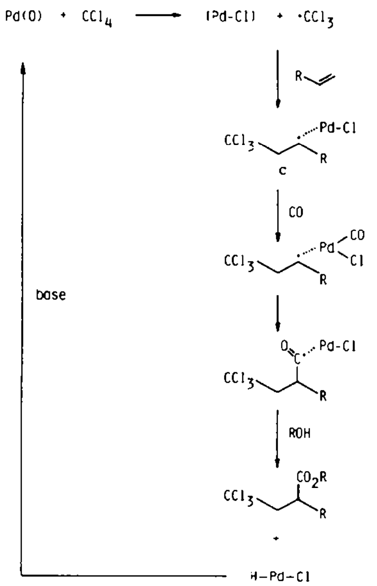
[b]. Diastereomer ratio determined by GLC.

Scheme 2.

expected trichloroacetates. No reaction was observed when CCl_3CO_2Me was used in place of CCl_4. Only the simple adduct was obtained with $BrCCl_3$.

Mechanism of the reaction

The Pd-catalyzed carbonylation of aryl, alkenyl and allyl halides is explained by oxidative addition of the halides, followed by CO insertion. However, as described in the preceding paper, a similar mechanism involving oxidative addition of CCl_4 followed by CO insertion is unlikely. In fact no carbonylation of CCl_4 takes place. Also we attempted the Pd-catalyzed reaction of bromobenzene with olefin under CO pressure in ethanol expecting the coaddition reaction. But bromobenzene reacted with olefin and CO separately to give styrene derivative and ethyl benzoate. Thus a mechanism involving radical species is more reasonable. As illustrated in Scheme 3, one electron transfer from Pd to CCl_4 produces trichloromethyl radical. The radical species **C** formed by the addition of trichloromethyl radical to olefin then reacts with CO to give the trichloro ester after alcoholysis. Facile incorporation of CO to the radical species **C** implies interaction or coordination of **C** with Pd.



Scheme 3.

EXPERIMENTAL

General

NMR spectra were taken at 60 MHz using a Hitachi R-24A spectrometer, or at 90 MHz using a Hitachi R-40 spectrometer. Chemical shifts are given in δ units (ppm) relative to tetramethylsilane. IR spectra were taken on a Jasco-IRA-2 spectrometer. The simple adducts **2**, **4**, **6**, **8** and **12** are well-known compounds. The esters **1** and **3** are known compounds[11] and identified by comparison of their spectral data with those of authentic samples. The new esters **5**, **7**, **9**, **10** and **11** were identified by their spectral data and elemental analyses.

General procedure for the coaddition reaction of CCl_4 *and* CO *to olefins*

A mixture of $Pd(OAc)_2$ (44 mg, 0.2 mmol), PPh_3 (104 mg, 0.4 mmol) and K_2CO_3 (2.76 g, 20 mmol) was placed in a stainless steel autoclave (100 ml). Olefin (20 mmol) and CCl_4 (10 ml) dissolved in EtOH (20 ml) were added, and then CO was introduced (40 atm). The soln was vigorously stirred at 50°. Efficient stirring was crucial. After 24 hr, K-salt was filtered off, and the filtrate was concentrated. The residue was purified by column chromatography (silica gel, hexane–ether) or distillation to afford the desired ester.

Ethyl 2-(2,2,2-trichloroethyl-3-(3,4-methylenedioxyphenyl)-propionate (**5**)

^{1}H-NMR (90 MHz, $CDCl_3$): δ 1.18 (t, 3H, J = 7 Hz, $OCH_2C\underline{H}_3$), 2.65–3.53 (m, 4H, $ArC\underline{H}_2CHC\underline{H}_2CCl_3$), 4.13 (q, 2H, J = 7 Hz, $OC\underline{H}_2CH_3$), 5.98 (s, 2H, $OC\underline{H}_2O$), 6.75 (s, 3H, phenyl); IR (neat) cm^{-1}: 2900, 1730, 1610, 800, 700. (Found: C, 47.33; H, 4.12; Cl, 29.78. Calc for $C_{14}H_{15}O_4Cl_3$: C, 47.55; H, 4.28; Cl, 30.08%.)

Methyl (10-ethoxycarbonyl)-12,12,12-trichlorododecanoate (**7**)

B.p. 155–160°/2 mmHg; ^{1}H-NMR (60 MHz, CCl_4): δ 1.05–1.8 (m, 17H, alkyl), 1.9–2.35 (m, 2H, $C\underline{H}_2CO_2Me$), 2.35–3.0 (m, 2H, CCl_3CH_2), 3.0–3.6 (m, 1H, $C\underline{H}CO_2Et$), 3.5 (s, 3H, OMe), 4.05 (q, 2H, J = 7 Hz, OCH_2); IR (neat) cm^{-1}: 2900, 1740, 790, 710. (Found: C, 49.15; H, 7.13; Cl, 26.96. Calc for $C_{16}H_{27}O_4Cl_3$: C, 49.31; H, 6.98; Cl, 27.29%.)

Diethyl 2-(2,2,2-trichloroethyl)glutarate (**9**)

B.p. 130–135°/2 mmHg; ^{1}H-NMR (60 MHz, CCl_4): δ 1.25 (t, 6H, J = 7 Hz, $C\underline{H}_3CH_2O$), 1.7–2.1 (m, 2H, methylene), 2.0–2.3 (m, 2H, $C\underline{H}_2CO_2Et$), 2.5–3.0 (m, 2H, CH_2CCl_3), 3.1–3.6 (m, 1H, $C\underline{H}CO_2Et$), 4.06 (q, 4H, J = 7 Hz, OCH_2); IR (neat) cm^{-1}: 2980, 1740, 785, 710. (Found: C, 41.04; H, 5.36; Cl, 33.33. Calc for $C_{11}H_{17}O_4Cl_3$: C, 41.34; H, 5.36; Cl, 33.28%.)

Ethyl 4,6,6,6-tetrachlorohexanoate (**10**)

B.p. 107°/2 mmHg; ^{1}H-NMR (60 MHz, CCl_4), 1.25 (t, 3H, J = 7 Hz, CH_3), 1.87–2.70 (m, 4H, $C\underline{H}_2C\underline{H}_2CO_2Et$), 3.2 (dd, 2H, J = 5, 2.5 Hz, CCl_3CH_2), 4.10 (q, 2H, J = 7 Hz, $OC\underline{H}_2CH_3$), 4.37 (m, 1H, CHCl); IR (neat) cm^{-1}: 2980, 1730, 785, 710 (Found: C, 34.38; H, 4.46; Cl, 51.78. Calc for $C_8H_{12}O_2Cl_4$: C, 34.07; H, 4.29; Cl, 50.29%.)

Ethyl 4,4,4-trichloro-2,3-dimethylbutanoate (**11**)

^{1}H-NMR (60 MHz, CCl_4), major isomer: δ 1.1–1.4 (m, 9H, CH_3), 2.9–3.4 (m, 2H, CCl_3CHCH), 4.1 (q, 2H, J = 7 Hz, OCH_2); minor isomer: 1.0–1.5 (m, 9H, CH_3), 2.4–2.8, 2.8–3.4

(m, 1H, 1H, CCl_3CHCH), 4.05 (q, 2H, OCH_2); IR (neat) cm^{-1}: 3000, 1740, 1190, 780.

REFERENCES AND NOTES

[1] J. Tsuji, *Organic Synthesis with Palladium Compounds*. Springer, Berlin (1980).

[2] J. Tsuji, J. Kiji, S. Imamura and M. Morikawa, *J. Am. Chem. Soc.* **86**, 4350 (1964).

[3] W. T. Dent, R. Long and G. H. Whitfield, *J. Chem. Soc.* 1588 (1964).

[4] D. Medema, R. van Helden and C. F. Kohll, *Inorg. Chim. Acta* **3**, 255 (1969).

[5] A. Shoenberg, I. Bartoletti and R. F. Heck, *J. Org. Chem.* **39**, 3318 (1974).

[6] J. K. Stille and P. K. Wong, *J. Org. Chem.* **40**, 532 (1975).

[7] H. Yoshida, N. Sugita, K. Kudo and Y. Takezaki, *Nippon Kagaku Zasshi* 1386 (1974).

[8] M. Hidai, T. Hikita, Y. Wada, Y. Fujikura and Y. Uchida, *Bull. Chem. Soc. Japan* **48**, 2075 (1975).

[9] T. Ito, K. Mori, T. Mizoroki and A. Ozaki, *Bull. Chem. Soc. Japan* **48**, 2091 (1975).

[10] A. Schoenberg and R. F. Heck, *J. Org. Chem.* **39**, 3327 (1974).

[11] T. Susuki and J. Tsuji, *Tetrahedron Lett.* 913 (1968); *J. Org. Chem.* **35**, 2982 (1970).

[12] R. E. Foster, A. W. Larchar, R. D. Lipscomb and B. C. Mckusick, *J. Am. Chem. Soc.* **78**, 5606 (1956).

[13] J. Tsuji, K. Sato and H. Nagashima, *Tetrahedron Lett.* **23**, 893 (1982).

[14] J. Tsuji, K. Sato and H. Nagashima, *Chem. Lett.* 1169 (1981); and *Tetrahedron* **41**, 393 (1985).