Tetrahedron Vol. 41, No. 2, pp. 393 to 397, 1985
Printed in Great Britain.

0040-4020/85 \$3.00 + .00
Pergamon Press Ltd.

PALLADIUM-CATALYZED ADDITION REACTION OF POLYHALOALKANES TO OLEFINS

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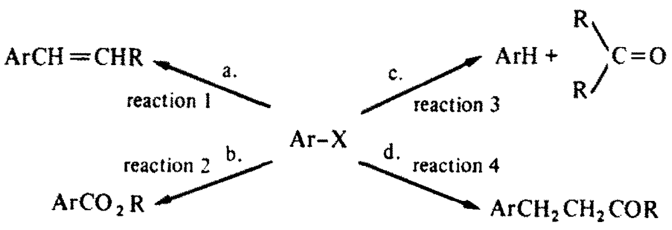
(*Received in Japan* 1 *May* 1984)

Abstract—$Pd(OAc)_2$ combined with phosphines catalyzes homolytic cleavage of the C—Cl bond of CCl_4 and $CCl_3CO_2CH_3$ leading to facile addition to olefins under mild conditions. $BrCCl_3$ also reacts with olefins to give 1,1,1-trichloro-3-bromoalkanes. The reaction is accelerated under CO atmosphere, and the presence of bases such as NaOAc or K_2CO_3 is essential to attain high yields of the adducts.

It is known that polyhalogenated methanes and homologues undergo homolytic cleavage of their carbon–halogen bond in the presence of free radical generators.[1,2] For example, dibenzoyl peroxide or AIBN initiates an addition reaction of CCl_4 to olefins via a radical chain mechanism to give 1,1,1,3-tetrachloroalkanes.[3] Furthermore, various transition metal salts or complexes act as catalysts for the addition reaction, and they show different features from the corresponding radical reactions.[4–6] Cu or Fe salts,[7,8] mono- or bi-nuclear metal carbonyls[9–12] and several metal phosphine complexes such as $RuCl_2(PPh_3)_3$[13–15] have been reported to be active for the addition reactions of CCl_4,[7,10–13,15] $BrCCl_3$,[15,16] $CCl_3CO_2CH_3$,[8,12,14] $CHCl_3$[17,18] and CCl_3CN[19] to olefins. Although the metal-catalyzed reactions are assumed to proceed *via* radical intermediates,[5,7,11,14] radical scavengers such as hydroquinone do not always inhibit the reaction.[7,13] This result indicates that simple free radical species might not be involved. Furthermore, some interesting features were observed in several reactions involving CO,[20,21] amines[22,23] or esters,[12,24,25] in which some transition metal salts or complexes are active catalysts.

In the chemistry of palladium, various organic halides undergo oxidative addition onto palladium involving carbon–halogen bond cleavage, and then react with olefins, alcohols or CO.[26,27] Reactions with aryl halides are summarized in Scheme 1. In reaction 1, insertion of the olefinic bond to the Pd—Ar bond and subsequent β-hydrogen elimination gives styryl derivatives.[28–30] Reaction 2 involves insertion of CO to the Ar—Pd bond, followed by alcoholysis to give esters.[31–33] As shown in reaction 3, oxidation of alcohols with aryl halides takes place in the absence of CO.[34,35] The reaction of allylic alcohols bearing the terminal olefinic bond gives rise to the formation of β-aryl ketones[36,37] (reaction 4). Although vinyl, allyl or benzyl halides take part in the above reactions besides aryl halides, little is known of the Pd-catalyzed reactions of polyhaloalkanes such as CCl_4, $BrCCl_3$ and $CCl_3CO_2CH_3$.



a. $RCH=CH_2$; b. CO, ROH; c. R_2CHOH; d. $CH_2=CHCH(OH)R$

Scheme 1. Palladium-catalyzed reactions of aryl halides.

We have found that Pd salts or complexes catalyze reactions of polyhaloalkanes with olefins,[15] CO,[20] alcohols[38] and allylic alcohols[39] in the presence of bases. Although we expected the similarity between Pd-catalyzed reactions of aryl halides and polyhalides, different results were obtained in the reactions with olefins and CO. As shown in Scheme 2, facile addition of polyhaloalkanes to olefins takes place, but no olefin formation is observed[15] (reaction 5). Under CO pressure in alcoholic media, γ,γ,γ-trichloro esters are obtained by coaddition of CCl_4 and CO to olefins[20] (reaction 6). Simple carbonylation of CCl_4 to form trichloroacetates does not occur. These results are similar to those observed under free radical conditions. On the other hand, Pd salts catalyze the oxidation of alcohols with CCl_4[38] (reaction 7) and γ,γ,γ-trichloro ketone formation from allylic alcohols bearing a terminal olefinic bond and CCl_4 or $BrCCl_3$[39] (reaction 8). These reactions show similarity to the Pd-catalyzed reactions of aryl halides.

We observed facile addition of CCl_4, $BrCCl_3$ and $CCl_3CO_2CH_3$ to various olefins under mild conditions with the three component system composed of $Pd(OAc)_2$, PPh_3 and K_2CO_3 or NaOAc.[15] This paper

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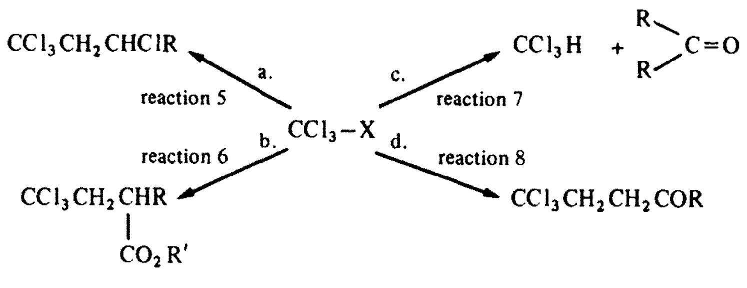


a. $RCH=CH_2$; b. $RCH=CH_2$, CO, R'OH; c. R_2CHOH; d. $CH_2=CHCH(OH)R$

Scheme 2. Palladium-catalyzed reactions of polyhalides.

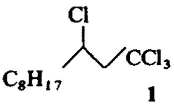
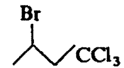
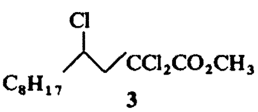
discloses full details of this addition reaction (Scheme 2, reaction 5).

RESULTS AND DISCUSSION

Activation of organic halides is known to be promoted by zero-valent Pd species. We investigated the reaction using $Pd(OAc)_2$ combined with phosphine ligands as a catalyst, which is believed to generate "$Pd(0)L_n$" species, *in situ*, under basic conditions.[26] We found that addition of CCl_4 to 1-decene proceeded at 100° to give 1,1,1,3-tetrachloroundecane (**1**) with the catalyst composed of $Pd(OAc)_2$ and phosphine. The presence of bases such as NaOAc and K_2CO_3 is essential to obtain **1** in high yields. Use of larger amounts of the base afforded higher yields, yields higher than 60% were obtained with two to three molar excesses of the base to olefin. Amines such as Et_3N and pyridine were not suitable, leading to the formation of ammonium salts. Amounts of phosphine also affected the yields of **1**. In the absence of PPh_3, **1** was scarcely formed, whereas excess of phosphine inhibited the reaction. Choice of ligands also influenced the yields to some extent. Phosphines gave better results than phosphites. Surprisingly, the reaction proceeded more readily under a CO atmosphere. In contrast to the facile carbonylation of aryl halides with Pd catalysts,[31–33] no incorporation of CO to either olefins or CCl_4 was observed, but obviously the reaction was accelerated. Similar or higher yields were obtained under a CO atmosphere at 80°. Formation of by-products, sometimes observed under argon atmosphere, was suppressed under CO.

From the point of view of synthetics, it is desirable that the reaction can be applied to a wide variety of organic compounds under mild conditions. In Table 1 are summarized the Pd-catalyzed reactions of various polyhaloalkanes with 1-decene. With Pd-catalysts, CCl_4, $BrCCl_3$ and $CCl_3CO_2CH_3$ underwent an addition reaction to 1-decene. Particularly, CCl_4 and $BrCCl_3$ reacted below 40° (entries 1–7). With other transition metal catalysts or under free radical conditions,[3] temperatures higher than 60–80° are usually required for the smooth addition reaction of CCl_4 and $BrCCl_3$.[7,10–16] In the reaction of $BrCCl_3$, high yields were attained even under argon atmosphere. $CCl_3CO_2CH_3$ reacted with 1-decene at 80–110° to give methyl 2,2,4-trichlorododecanoate (**3**) in yields of about 60% (entries 8 and 9). In this reaction, clear acceleration by CO was observed. Formation of α,α-dichloro-γ-butyrolactones reported in the previous report with $Cp_2Fe_2(CO)_4$ or $Cp_2Mo_2(CO)_6$[12] were not observed with the Pd catalyst. Limitation of the Pd catalyst was observed in the reaction of CCl_3CN and

Table 1. Addition reaction of polyhaloalkanes to 1-decene*

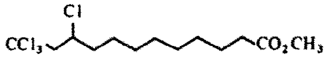
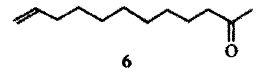
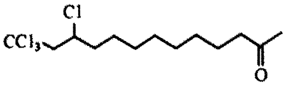
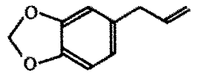
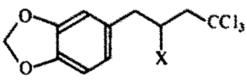
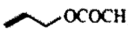
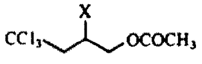
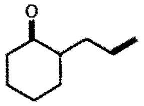
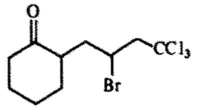
Entry	Polyhaloalkane (eq.)†	Temp (°)	Time (hr)	Atmosphere	Product	Yield (%)‡
1	CCl_4 (5)	100	5	Ar	 **1**	77
2	CCl_4 (5)	100	3	Ar		(54)
3	CCl_4 (5)	80	3	CO		(60)
4	CCl_4 (5)	40	5	CO		(20)
5	CCl_4 (5)	r.t.	120	CO		90
6	$BrCCl_3$ (1)	40	5	Ar	 **2**	(88)
7	$BrCCl_3$ (2)	100	3.5	Ar		90
8	$CCl_3CO_2CH_3$ (5)	100	15	Ar	 **3**	64
9	$CCl_3CO_2CH_3$ (5)	80	7	CO		62

* All reactions were carried out in the presence of $Pd(OAc)_2$ (1 mol%), PPh_3 (2 mol%), and K_2CO_3 (200 mol%).

† Amounts of polyhaloalkanes based on the olefin applied.

‡ Figures in parentheses are the yields determined by GLC using diphenyl as an internal standard. Others are isolated yields.

Table 2. Addition reaction of CCl_4 or $BrCCl_3$ to Functionalized Olefins*

Entry	Olefin	Polyhalide	Temp (°)	Time (hr)	Product	Yield (%)
1.	 4	CCl_4	80	5	 5	58
2.	 6	CCl_4	110	20	 7	71
3.	 8	CCl_4 $BrCCl_3$	110 80	38 9	 9 (X=Cl), 10 (X=b Br)	39 52
4.	 11	CCl_4 $BrCCl_3$	110 80	22 7	 12 (X=Cl), 13 (X=Br)	20 83
5.	 14	$BrCCl_3$	80	8	 15	65

* All reactions were carried out in the presence of $Pd(OAc)_2$ (1 mol%), PPh_3 (2 mol%) and K_2CO_3 (200 mol%) under CO atmosphere.

$CHCl_3$. Even at higher temperatures and for prolonged reaction time applied, CCl_3CN afforded the adducts in yields lower than 40%. While, $CHCl_3$ afforded a complicated mixture.

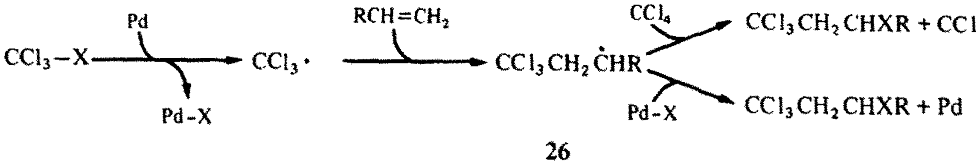
Pd-catalyzed reactions of CCl_4 or $BrCCl_3$ to olefins bearing ester, ketone or ether group under optimal conditions described above are summarized in Table 2. Methyl 10-undecenoate (**4**) or 11-dodecen-2-one (**6**) readily reacted with CCl_4 to give the corresponding adducts **5** or **7**. In the reaction of safrole (**8**) or allyl acetate (**11**), CCl_4 afforded the adducts **9** or **12** in low yields, but $BrCCl_3$ reacted to give **10** or **13** in high yields (entries 3 and 4). Similarly, 2-allylcyclohexanone (**14**) reacted with $BrCCl_3$ to afford **15** in yield of 65%, but a satisfactory result was not obtained with CCl_4.

High reactivity of $BrCCl_3$ in the free radical addition reaction is well known.[1] With the Pd catalyst, $BrCCl_3$ also reacts with olefins more readily than CCl_4. Since the adduct was obtained in high yields with only one equivalent of $BrCCl_3$ to olefins, the 1 : 1 adduct can be selectively prepared from dienes. The terminal olefinic bond of 4-vinylcyclohexene selectively reacted with $BrCCl_3$ to give 3-(1-bromo-3,3,3-trichloropropyl) cyclohexene as the 1 : 1 adduct with a 57% yield. From 1,7-octadiene, 3-bromo-1,1,1-trichloro-8-nonene as the 1 : 1 adduct, was predominantly formed over 3,8-dibromo-1,1,1,10,10,10-hexachlorodecane as the 1 : 2 adduct in yields of 51% and 10%, respectively. They were easily separated by column chromatography.

The ratio of diastereomers formed in the addition reaction of polyhaloalkanes to internal olefinic bonds is of interest from a mechanistic point of view. Addition of CCl_4 and $BrCCl_3$ to cyclohexene under free radical conditions gave almost equimolar mixtures of *cis*- and *trans*-adducts.[40] The same tendency was observed with the Pd catalyst. On the other hand, high *trans* selectivity was observed in the Ru-catalyzed addition reaction of CCl_4 to cyclohexene.[41] An approximately 4 : 1 diastereomeric mixture of 2-methyl-1,1,1,3-tetrachlorobutane and 3-bromo-2-methyl-1,1,1-trichlorobutane was formed from either *cis*- or *trans*-2-butene under free radical conditions or by the catalysis of Cu.[7,42] With the Pd catalyst, diastereomer ratios similar to those observed under free radical conditions were obtained.

A mechanism of the Pd-catalyzed reaction of polyhaloalkanes with olefins involving oxidative addition of R—X onto Pd,[43,44] followed by insertion of olefins, is unlikely. Attempts to isolate a Pd complex formed by oxidative addition of polyhaloalkanes onto Pd failed. Tayim and Akl[45] reported that $Pd(PPh_3)_4$ reacted with CCl_4 to give $PdCl_2(PPh_3)_2$. This result indicates that oxidation of Pd(0) with CCl_4, probably *via* one electron transfer from Pd(0) to CCl_4, takes place easily. This oxidation is considered to cause deactivation of the catalyst in the addition reaction of polyhaloalkanes. Our finding that the addition of bases was essential or acceleration was observed under a CO atmosphere can be explained by the fact that Pd(II) species formed by the oxidation undergo reduction with bases or CO to zero-valent state.[26,30–33]

We propose the mechanism illustrated in Scheme 3. One electron transfer from Pd(0) to polyhaloalkanes gives a trichloromethyl radical which adds to olefins to



Scheme 3. Mechanism of the palladium-catalyzed addition reaction of polyhaloalkanes to olefins.

form the radical **26**, which then abstracts chlorine from either polyhaloalkanes or Pd—Cl. In the former case, the radical chain reaction is initiated, and in the latter case, the active Pd catalyst is regenerated.

EXPERIMENTAL

General

NMR spectra were taken at 60 MHz using a Hitachi R-24A spectrometer. Chemical shifts are given in δ units, ppm relative to TMS as an internal standard. IR spectra were taken on a Jasco-IR-2 spectrometer and recorded in cm^{-1}. Compounds **1**,[43] **3**,[46] **5**,[47] **12**,[48] **21**,[41] **22**,[41] **23**,[7] **24**,[42] and **25**,[16] were identified by comparing their spectral data with those of authentic samples. Other products were identified by spectral data and elemental analyses as shown below.

General procedure of the addition reaction of CCl_4 *to olefins*

Method A. $Pd(OAc)_2$ (2 mg, 0.01 mmol), PPh_3 (5 mg, 0.02 mmol) and K_2CO_3 (276 mg, 2 mmol) were placed in a Pyrex tube fitted with a screw cap, the atmosphere was replaced by argon. Olefin dissolved in CCl_4 (1 ml) was introduced, and the mixture was heated at 100° for 3 hr. The mixture was poured into cold HCl aq and extracted with benzene. The combined organic layer was washed with $NaHCO_3$ aq and brine and dried over $MgSO_4$. After concentration, chromatographic separation of the residue afforded the desired tetrachloride.

Method B. The reaction was carried out in a flask fitted with a reflux condenser and a rubber balloon filled with CO. After gentle reflux for several hours, the mixture was treated as described above to give the desired product.

11,13,13,13-*Tetrachlorotridecan-2-one* (**7**). NMR (CCl_4) 1.1–2.0 (m, 14H, alkyl), 2.15 (s, 3H, Ac), 2.2–2.6 (m, 2H, CH_2CO), 3.1–3.4 (m, 2H, CCl_3CH_2), 4.0–4.5 (m, 1H, CHCl); IR (neat) 2950, 1720, 1380, 790, 710. (Found: C, 46.55; H, 6.57. Calc for $C_{13}H_{22}OCl_4$: C, 46.45; H, 6.60%.)

1,2-*Methylenedioxy* - 4 - (2,4,4,4 - *tetrachlorobutyl*)*benzene* (**9**). NMR (CCl_4) 3.05 (q, 2H, CH_2CCl_3), 3.15 (d, 2H, J = 5 Hz, $ArCH_2$), 4.32 (quintet, 1H, J = 5 Hz, CHCl), 5.90 (s, 2H, OCH_2O), 6.65 (s, 3H, phenyl); IR (neat) 2900, 1610, 1050, 800. (Found: C, 41.96; H, 3.12; Cl, 44.21. Calc for $C_{11}H_{10}O_2Cl_4$: C, 41.81; H, 3.19; Cl, 44.88%.)

General procedure for the addition reaction of $BrCCl_3$ *to olefins*

The reaction was carried out in the same manner as decribed in procedure B. A benzene solution of equimolar or two-molar amounts of $BrCCl_3$ for the olefin was employed.

3-*Bromo*-1,1,1-*trichloroundecane* (**2**). NMR (CCl_4) 0.7–1.1 (m, 3H, CH_3), 1.1–2.3 (m, 14H, alkyl), 2.9–3.7 (m, 2H, CCl_3CH_2), 4.0–4.5 (m, 1H, CHBr); IR (neat) 2920, 1460, 790, 700.

1,2 - *Methylenedioxy* - 4 - (2 - *bromo* - 4,4,4 - *tricholorobutyl*)*benzene* (**10**). NMR (CCl_4) 2.8–3.5 (m, 4H, $ArCH_2$, CCl_3CH_2), 4.05–4.6 (m, 1H, CHBr), 5.9 (s, 2H, OCH_2O), 6.7 (s, 3H, phenyl); IR (neat) 2900, 1500, 1440, 1250, 1040, 940, 800, 700. (Found: C, 36.78; H, 2.70; Br + Cl, 52.04. Calc for $C_{11}H_{10}O_2BrCl_3$: C, 36.65; H, 2.80; Br + Cl, 51.67%.)

2-*Bromo*-4,4,4-*trichlorobutyl acetate* (**13**). NMR (CCl_4) 2.05 (s, 3H, Ac), 3.2–3.5 (m, 2H, CCl_3CH_2), 4.1–4.7 (m, 1H, BrCH), 4.35 (m, 2H, OCH_2); IR (neat) 1750, 1230, 1050, 800, 700. (Found: C, 24.18; H, 2.54. Calc for $C_6H_8O_2BrCl_3$: C, 24.15; H, 2.70%.)

2 - (2 - *Bromo* - 4,4,4 - *trichlorobutyl*)*cyclohexanone* (**15**). NMR (CCl_4) 0.7–2.85 (m, 11H, alkyl), 2.85–3.8 (m, 2H, CCl_3CH_2), 3.9–4.8 (m, 1H, BrCH); IR (neat) 2930, 1710, 1440, 790, 700. (Found: C, 36.09; H, 4.21. Calc for $C_{10}H_{12}OBrCl_3$: C, 35.70; H, 4.19%.)

3 - (1 - *Bromo* - 3,3,3 - *trichloropropyl*)*cyclohexene*. NMR (CCl_4) 1.2–1.4 (m, 7H, alkyl), 3.32 (dd, 2H, J = 4, 5 Hz, CCl_3CH_2), 4.2–4.5 (m, 1H, CHBr), 5.7 (s, 2H, olefinic); IR (neat) 2950, 1450, 795. (Found: C, 35.45; H, 3.97. Calc for $C_9H_{12}BrCl_3$; C, 35.27; H, 3.95%.)

3-*Bromo*-1,1,1-*trichloro*-8-*nonene*. NMR (CCl_4) 1.1–2.4 (m, 8H, alkyl), 3.15–3.45 (m, 2H, CH_2CCl_3), 4.05–4.5 (m, 1H, CHBr), 4.7–6.0 (m, 3H, olefinic); IR (neat) 2905, 1640, 910, 790, 700. (Found: C, 34.31; H, 4.50. Calc for $C_9H_{14}BrCl_3$: C, 35.04; H, 4.57%.)

3,8 - *Dibromo* - 1,1,1,10,10,10 - *hexachlorodecane*. NMR (CCl_4) 1.0–1.4 (m, 8H, alkyl), 2.9–3.7 (m, 4H, CH_2CCl_3), 4.0–4.5 (m, 2H, BrCH); IR (neat) 2850, 790, 700. (Found: C, 23.98; H, 2.68; Br + Cl, 73.12. Calc for $C_{10}H_{14}Br_2Cl_6$: C, 23.70; H, 2,78; Br + Cl; 73.51%.) Addition reaction of $CCl_3CO_2CH_3$ was carried out by a similar procedure to that used in method A.

Methyl 2,2,4-*trichlorododecanoate* (**3**). NMR (CCl_4) 0.7–1.1 (m, 3H, CH_3), 1.1–2.2 (m, 14H, alkyl), 2.6–3.4 (m, 2H, CCl_3CH_2), 3.9 (s, 3H, OCH_3), 4.0–4.4 (m, 1H, CHCl); IR (neat) 2930, 1770, 1340, 1250, 1020, 840, 770.

Addition of CCl_4 *or* $BrCCl_3$ *to cyclohexene*. A mixture of cyclohexene (410 mg, 5 mmol) and $BrCCl_3$ (1 g, 5 mmol) dissolved in benzene was heated at 80° in a Pyrex tube fitted with a screw cap, in the presence of $Pd(OAc)_2$ (10 mg, 0.05 mmol), PPh_3 (26 mg, 0.1 mmol) and K_2CO_3 (690 mg, 5 mmol) in an argon atmosphere. After 5 hr, 469 mg, of 1-(trichloromethyl)-2-bromocyclohexane was obtained. Similarly, the adduct was obtained in yields of 10% with 25 mmol of CCl_4 at 100° for 20 hr.

Addition of CCl_4 *or* $BrCCl_3$ *to* cis- *or* trans-2-*butene*. A mixture of CCl_4 (5 ml), *cis*-2-butene (1 ml), $Pd(OAc)_2$ (10 mg, 0.05 mmol) and K_2CO_3 (690 mg, 5 mmol) in a Pyrex tube fitted with a screw cap, was heated at 100° in an argon atmosphere for 5 hr. After the usual work-up, 487 mg of 2-methyl-1,1,1,3-tetrachlorobutane was obtained. 243 mg of the adduct was obtained from *trans*-2-butene. When the reaction was carried out using $BrCCl_3$ (1 g, 5 mmol) instead of CCl_4, 1.12 g of 3-bromo-2-methyl-1,1,1-trichlorobutane from *cis*-2-butene and 954 mg from *trans*-2-butene were obtained.

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