CHEMISTRY LETTERS, pp. 1605-1608, 1981.

ACTIVATION OF POLYHALOALKANES BY PALLADIUM CATALYST. PREPARATION OF γ-TRICHLORO KETONES BY THE PALLADIUM CATALYZED ADDITION REACTION OF BROMOTRICHLOROMETHANE AND CARBON TETRACHLORIDE TO ALLYL ALCOHOLS

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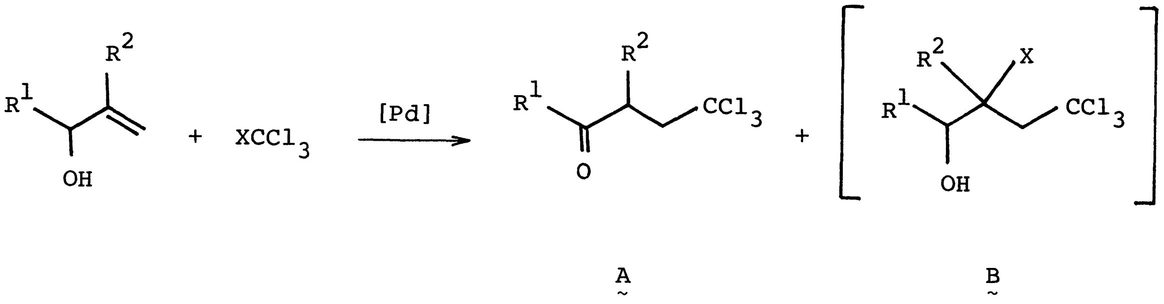
The palladium catalyzed reaction of $BrCCl_3$ and CCl_4 with allyl alcohols with terminal double bonds afforded γ-trichloro ketones. $Pd(OAc)_2$ combined with tri-*o*-tolylphosphine in the presence of a base gave the best results.

Addition reaction of polyhaloalkanes to olefins takes place easily via homolytic cleavage of carbon-halogen bond. Although many radical initiators$^{1)}$ and transition metal complexes$^{2-5)}$ reportedly exhibit catalytic activity in this reaction, few studies have been carried out on the addition reaction of $BrCCl_3$ and CCl_4 to allyl alcohols. Only the reaction of allyl alcohol (1-propen-3-ol) with CCl_4 catalyzed by $FeCl_3$ was performed by Asscher et al who reported the formation of 1,1,1,3-tetrachlorobutan-4-ol as the usual 1 : 1 adduct in 55% yield.$^{2)}$ Recently we have found that palladium phosphine complexes are excellent catalysts for the reaction of $BrCCl_3$ and CCl_4 with olefins to afford 1,1,1-trichloro-3-bromoalkanes and 1,1,1,3-tetrachloroalkanes, respectively, in high yields under mild conditions.$^{6)}$ In the course of further studies on the palladium catalyzed activation of polyhaloalkanes, we found unexpectedly that 1,1,1-trichloro-4-alkanones **A** were formed in high yields by the palladium catalyzed reaction of $BrCCl_3$ and CCl_4 with certain allyl alcohols, and only a small amount of the usual 1 : 1 adducts **B** was detected. In this paper, we wish to report results of this palladium catalyzed reaction of allyl alcohols.

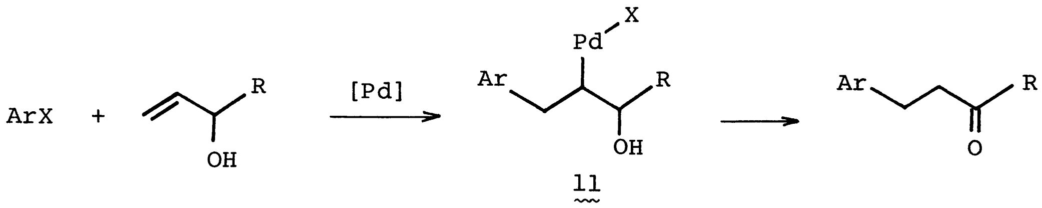


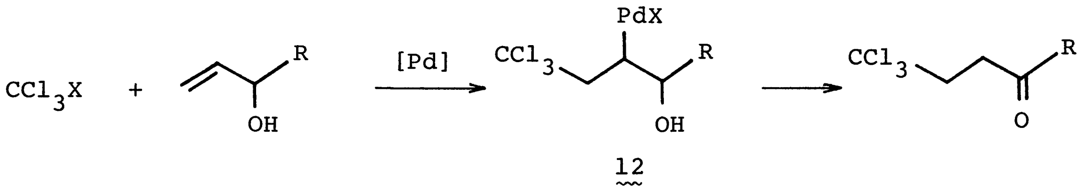
X = Cl, Br

We carried out the reaction of 1-hepten-3-ol (1) and other allyl alcohols with an equimolar amount of $BrCCl_3$ in the presence of $Pd(OAc)_2$/tri-*o*-tolylphosphine [(*o*-Tol)$_3$P] (1 : 2, 1-5 mol%) and K_2CO_3 (2 equiv.) in benzene at 110°C, and obtained 1,1,1-trichloro-4-octanone (6) and similar trichloro ketones in 40-90% yields, respectively. The same ketones were obtained by the use of five equivalents of CCl_4 instead of $BrCCl_3$, but in somewhat lower yields. (entries 1-ii, 5-iii) A significant ligand effect was observed as listed in entries 1-iii and 1-iv. P(*o*-Tol)$_3$ showed the better activity than PPh_3. In the absence of the phosphine, the reaction scarecely occurred. The course of the reaction also depends on the structure of allyl alcohols. 2-Alkyl-1-alken-3-ols, such as 4 and 5, were easily converted to the corresponding ketones even at 40°C, whereas the formation of ketones from 1-alken-3-ols, such as 1, 2, and 3, required elevated temperature. (110°C) Reactions of allyl alcohols with primary hydroxy group such as cinnamyl alcohol, 1-propen-3-ol, and 2-phenyl-1-propen-3-ol afforded a mixture of carbonyl compounds. These results can be explained by the occurrence of facile palladium catalyzed oxidation of primary hydroxy group with $BrCCl_3$ and CCl_4 before the introduction of trichloromethyl group.7) We have already reported that the presence of a base is quite important for the palladium catalyzed addition reaction of polyhaloalkanes to olefins.6) In this reaction, we also observed no reaction in the absence of the base. The best yields were obtained by adding K_2CO_3 as the base, and Bu_3N and NaOAc afforded the ketones in lower yields.

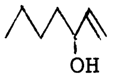
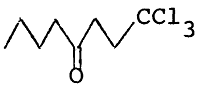
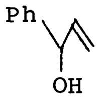
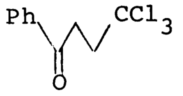
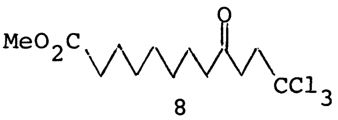
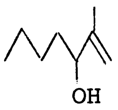
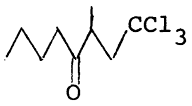
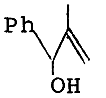
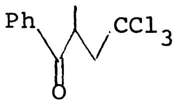
We investigated the reaction of $BrCCl_3$ with 1 using other catalysts which are known to have a good catalytic activity in the addition reaction of polyhaloalkanes to olefins. The 1 : 1 adduct was formed in high yields by using $RuCl_2(PPh_3)_3$ and $(PhCO_2)_2$ as the catalysts, whereas a mixture of several products with complete absence of the ketone 6 was obtained by using CuCl as the catalyst. Thus, the ketone formation is specific to the palladium catalyst.

It is known that aryl iodides and bromides readily react with allyl alcohols to afford 1-aryl-3-alkanones in high yields by the catalysis of palladium phosphine complexes, and the reaction is believed to proceed through the formation of σ-alkylpalladium complex 11 as an intermediate and the subsequent β-hydride elimination.8,9) The reaction described in this paper seems to proceed through a similar intermediate 12.





Table

			CCl_3X[a]	PR_3[b]	Temp (°C)	Time (h)	Cat (%)	Products	Yield (%)[c]
1	 1	i.	Br	T	110	3	5	 6	66
		ii.	Cl	T	110	18	5		39
		iii.	Br	T	110	3	5		(62)[d]
		iv.	Br	P	110	3	5		(26)[d]
2	 2		Br	T	110	4	1	 7	43
3	 3		Br	T	110	4	5	 8	47
4	 4		Br	T	40	13	1	 9	80
5	 5	i.	Br	T	40	8	1	 10	55
		ii.	Br	T	110	4	1		87
		iii.	Cl	T	110	7	1		50

[a] Br = $BrCCl_3$, Cl = CCl_4.
[b] T = $(o\text{-Tol})_3P$, P = PPh_3.
[c] Isolated yields.
[d] Determined by G.L.C..

General procedure

In a pyrex test tube with a screw cap, were placed $Pd(OAc)_2$ (2 mg, 0.01 mmol), $P(o\text{-Tol})_3$ (6 mg, 0.02 mmol) and K_2CO_3 (276 mg, 2 mmol) under argon atmosphere. A benzene solution of allyl alcohol (1 mmol) and $BrCCl_3$ (198.3 mg, 1 mmol) was added and the mixture was heated at 110°C for several hours. After the usual work-up and purification by column chromatography, the corresponding ketone was obtained.

References

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10) Spectral data of the ketones obtained by this reaction.

6: IR (neat) 1720, 780, 690 cm^{-1}; NMR ($CDCl_3$, TMS) δ 0.7-1.1 (m, 3 H, CH_3), 1.1-1.9 (m, 4 H, alkyl), 2.33-2.70 (m, 2 H, $\underline{CH_2}CO$), 2.70-3.20 (m, 4 H, $CO\underline{CH_2}\underline{CH_2}CCl_3$); m/e 230 (M), 232 (M+2), 234 (M+4).

7: IR (neat) 1690, 1600, 1580, 750, 690 cm^{-1}; NMR ($CDCl_3$, TMS) δ 3.0-3.7 (m, 4 H, $CO\underline{CH_2}\underline{CH_2}CCl_3$), 7.3-8.25 (m, 5 H, phenyl); m/e 250 (M), 252 (M+2), 254 (M+4).

8: IR (neat) 1735, 1715, 780, 690 cm^{-1}; NMR ($CDCl_3$, TMS) δ 1.15-1.8 (m, 10 H, alkyl), 2.31 (t, 2 H, J = 7.5 Hz, $\underline{CH_2}CO_2Me$), 2.48 (t, 2 H, J = 7.5 Hz, $\underline{CH_2}CO$), 2.87-3.20 (m, 4 H, $CO\underline{CH_2}\underline{CH_2}CCl_3$), 3.68 (s, 3 H, OCH_3); m/e 330 (M), 332 (M+2), 334 (M+4).

9: IR (neat) 1720, 770, 700 cm^{-1}; NMR ($CDCl_3$, TMS) δ 0.8-1.1 (m, 3 H, CH_3), 1.1-1.8 (m, 4 H, alkyl), 1.23 (d, 3 H, J = 7.5 Hz, $\underline{CH_3}CHCO$), 2.4-2.76 (m, 3 H, $CCl_3\underline{CH_a}$, $CO\underline{CH_2}$), 3.1 (m, 1 H, CHCO), 3.6 (dd, 1 H, J = 7.5, 15 Hz, $CCl_3\underline{CH_b}$); m/e 244 (M), 246 (M+2), 248 (M+4).

10: IR (neat) 1680, 1600, 1580, 780, 743, 705 cm^{-1}; NMR ($CDCl_3$, TMS) δ 1.31 (d, 3 H, J = 7.5 Hz, CH_3), 2.75 (broad d, 1 H, $CCl_3\underline{CH_a}$), 3.63-4.20 (m, 2 H, $CCl_3\underline{CH_b}\underline{CH}CO$), 7.35-8.25 (m, 5 H, phenyl); m/e 264 (M), 266 (M+2), 268 (M+4).

(Received September 16, 1981)