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Dehydrogenation of Ketones by Palladium(II) trifluoroacetate -Phosphine and -Sulfide Systems

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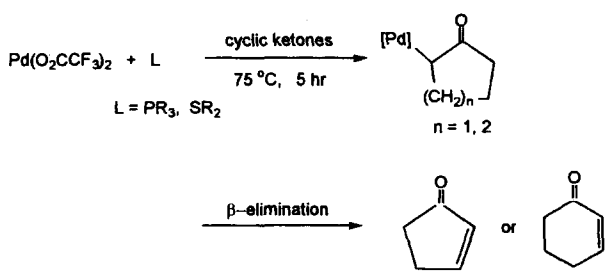
Received June 10, 1997

Activation of carbon-hydrogen bonds is an important subject in organometallic chemistry. We have investigated the activation of aromatic carbon-hydrogen bond by $Pd(OAc)_2$-phosphine system and have showed the system to be more effective than $Pd(OAc)_2$-sulfide system.[1] Herein, we wish to report the activation of aliphatic carbon-hydrogen bond of cyclic ketones (cyclopentanone and cyclohexanone) using $Pd(CF_3CO_2)_2$-phosphine and -sulfide systems. Although many papers on the activation of aliphatic C-H bond have been published previously[2-5] and dehydrogenation reactions of cyclic ketones were studied by Fuchita *et al.* using Pd $(OAc)_2$-SBu^i_2 system,[6] trifluoroacetate as an anion is an interesting choice for the following reasons: 1) the $CF_3CO_2^-$ ion is relatively weaker than $CH_3CO_2^-$ ion in basicity and M-O_2CCF_3 bond is quite labile,[2,7] which can be dissociated more easily to give a vacant site of the metal complexes, 2) however, trifluoroacetate ligand might reduce the catalytic activity due to the poor basicity as well, and 3) trifluoroacetate does not contain C-H bond itself. Also, phosphine has been selected to compare the catalytic activity with the sulfide system. The reaction of cyclic ketone has been carried out for 5 hours in the presence of $Pd(CF_3CO_2)_2$ with phosphine or sulfide (PR_3=P(p-$C_6H_4CH_3$)$_3$, P(p-C_6H_4F)$_3$, PPh_3, P(OBu^n)$_3$ and SR_2=S($CH_2CH_2CH_3$)$_2$, S{$CH(CH_3)_2$}$_2$, S{$CH(CH_3)(C_2H_5)$}$_2$, S(CH_2Ph)$_2$, S{$C(CH_3)_3$}$_2$) at 75 °C in this work. The mechanism of deydrogenation of cyclic ketones is considered to be the formation of α-palladated cyclic ketone followed by the formation of dehydrogenation product from β-hydride elimination.[6]



The yield of 2-cyclohexen-1-one produced from cyclohexanone is highest (589%) when the molar ratio of Pd $(CF_3CO_2)_2$ to P(p-$C_6H_4CH_3$)$_3$ is 1 : 2, while the highest yield was obtained for the molar ratio of 1 : 2/3 in $Pd(OAc)_2$-SBu^i_2 system. The yields based on the amount of $Pd(CF_3CO_2)_2$ used are the average value of three or four trials and have been measured on GC with hexadecane as an internal standard. Lower yields were obtained for the ratio of 1 : 2/3 (417%), 1 : 1 (513%) and others. Therefore, the molar ratio has been kept 1 : 2 for all of the reactions in this work to maintain the identical reaction condition. Although it is not clear for now, the ratio of 1 : 2 may suggest the structure of the intermediate involves two phosphine ligands coordinated to a palladium metal. Table 1 shows the yields of cycloalkenones catalyzed by $Pd(CF_3CO_2)_2$-phosphine and -sulfide systems. In dehydrogenation reaction of cyclohexanone, the highest yield (589%) of 2-cyclohexen-1-one has been afforded by P(p-$C_6H_4CH_3$)$_3$, which includes the most basic substituent among the series of phosphines. It is interesting to point out P(p-C_6H_4F)$_3$ gives more yield (363%) than PPh_3 (307%). The *para*-fluorine of the phenyl group seems to be rather electron donating than electron withdrawing due to the resonance effect. Yield is 275% in the absence of phosphine, which means $Pd(CF_3CO_2)_2$ itself can activate the aliphatic C-H bond of ketone very well. For reference, the same reaction using $Pd(OAc)_2$ was carried out under the identical condition, and the yield is extremely low (28%), therefore, trifluoroacetate anion reinforces catalytic activity more than acetate does. On the other hand, P(OBu^n)$_3$ containing an electronegative and bulky substituent gives much lower yield (39%) than $Pd(CF_3CO_2)_2$ itself. Therefore, more basic and less hindered phosphines[8] afford more products.

In case of sulfide series, S($CH_2CH_2CH_3$)$_2$ affords the highest yield (422%) and the second yield (320%) is obtained for S{$CH(CH_3)_2$}$_2$ and SPh_2 gives 223% of the yield. It seems the sulfide with more basic substituent gives more yield than phosphine series. However, steric factor must be

Table 1. Yields of Cycloalkenones by $Pd(CF_3CO_2)_2$-Phosphine and -Sulfide Systems[a]

Product	Phosphine	Yield (%)[b]	Sulfide	Yield (%)[b]
2-cyclohexen-	$P(p\text{-}C_6H_4CH_3)_3$	589	$S(CH_2CH_2CH_3)_2$	422
1-one	$P(p\text{-}C_6H_4F)_3$	363	$S\{CH(CH_3)_2\}_2$	320
	PPh_3	307	SPh_2	223
	$P(OBu^n)_3$	39	$S(CH_2Ph)_2$	57
	None	275	$S\{C(CH_3)_3\}_2$	51
2-cyclopenten-	$P(p\text{-}C_6H_4CH_3)_3$	200	$S(CH_2CH_2CH_3)_2$	133
1-one	$P(p\text{-}C_6H_4F)_3$	195	$S\{CH(CH_3)_2\}_2$	134
	PPh_3	164	$S\{CH(CH_3)(C_2H_5)\}_2$	93
	$P(OBu^n)_3$	85	$S(CH_2Ph)_2$	57
	None	161	$S\{C(CH_3)_3\}_2$	45

[a] Reaction conditions: $Pd(CF_3CO_2)_2$, 50 mg (0.163 mmol); phosphines and sulfides, 2 molar equivalents to $Pd(CF_3CO_2)_2$; cycloalkanone 5.0 mL; 70 °C for 5 h. [b] Calculated based on Pd $(CF_3CO_2)_2$.

also important since the sulfides with bulky substituents such as $S\{C(CH_3)_3\}_2$ and $S(CH_2Ph)_2$ give very low yield, 51% and 57% respectively. Although direct comparison between the effect of phosphine and sulfide is not available from this data due to the different subsituents, phosphines seems to show better catalytic activity than sulfide from the results of PPh_3 (307%) and SPh_2 (223%), containing the same phenyl substituent.

The effect of the substituents of both phosphines and sulfides on the yield of 2-cyclopenten-1-one is similar to the case of 2-cyclohexen-1-one except the yield of 2-cyclohexen-1-one being higher for the same catalytic system. In the phosphine series, the highest yield of 2-cyclopenten-1-one has been obtained for $P(p\text{-}C_6H_4CH_3)_3$ (200%) and $P(p\text{-}C_6H_4F)_3$ (195%) gives more yield than PPh_3 (164%), again. The product has been formed in good yield (161%) for Pd $(CF_3CO_2)_2$ only. Addition of sulfide does not seem to increase the catalytic activity of $Pd(CF_3CO_2)_2$, in fact, decrease the activity in this case. However, $S(CH_2CH_2CH_3)_2$ and $S\{CH(CH_3)_2\}_2$ systems act as catalysts since the yield of the product is over 100%. $Pd(OAc)_2$-SBu^i_2 system affords 412% yield of 2-cyclopenten-1-one and 371% of 2-cyclohexen-1-one, but the yields were so low for other sulfides that data was available only for SBu^i_2.[6]

In conclusion, 1) trifluoroacetate is a good choice as an anion since $Pd(CF_3CO_2)_2$ itself catalyzes the C-H bond activation very well, and both $Pd(CF_3CO_2)_2$-phosphine and Pd $(CF_3CO_2)_2$-sulfide systems act as reasonably good catalysts compared with $Pd(OAc)_2$-sulfide system, 2) phosphines or sulfides containing more basic and less hindered substituents increase the yield of the product and 3) $Pd(CF_3CO_2)_2$-phosphine system seems to catalyze more effectively than $Pd(CF_3CO_2)_2$-sulfide system. 4) 2-cyclohexen-1-one is obtained in more yield than 2-cyclopenten-1-one.

Experimental

Materials. Palladium trifluoroacetate, phosphines, sulfides, 1-cyclopentanone and 2-cyclohexanone purchased from Aldrich were all reagent-grade and were used without further purification. Hexane was distilled over sodium at reflux under N_2 just prior to use.

Measurements. Reactions were carried out using 50 mg (0.163 mmol) of $Pd(CF_3CO_2)_2$, 0.326 mmol of phosphine or sulfide in 5 mL of cycloalkanone at 70 °C under O_2 for 5 h. After decanting the solution, hexane was added to remove the palladium metal by precipitation and the residue was filtered off. The collected solution was analyzed by Hewlett Packard 5890 Series II spectrometer on a HP-5 column.

Acknowledgment. This work was supported by Korea Science and Engineering Foundation (951-0303-082-2).

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