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Preliminary communication

PALLADIUM COMPLEX CATALYZED CARBONYLATION OF ORGANIC HALIDES HAVING β-HYDROGENS

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Summary

α-Phenylethyl bromide, ethyl α-bromopropionate, and α-phenylpropyl bromide were smoothly converted to the corresponding methyl ketones by treatment with carbon monoxide and palladium complex catalysts in the presence of tetramethyltin. This is the first case of successful carbonylation of organic halides having β-hydrogens. Triphenylarsine was found to be a better ligand than triphenylphosphine to promote carbonylation.

Carbonylation of organic halides is a very important and useful method to prepare the corresponding acids, esters, amides, and aldehydes [1—6]. However, the carbonylation with palladium complexes can be successfully applied only to organic halides such as aromatic, heteroaromatic, vinylic, allylic, and benzylic halides, all of which do not undergo facile β-elimination. Previously, we reported the successful ketonization of organic halides with carbon monoxide and organotin compounds [7]. We now wish to report that this carbonylation can be applied to those halides in which a halogen atom is bound to an sp^3-carbon atom adjacent to a methyl or methylene group, using tripenylarsine as an effective ligand.

The results are summarized in Table 1.

In a typical procedure, a 27 ml stainless steel autoclave was charged with α-phenylethyl bromide (7.5 mmol), tetramethyltin (3.75 mmol), $PdCl_2(PPh_3)_2$ (1.25×10^{-2} mmol), and 3 ml of HMPA, and was pressurized up to 20 atm with carbon monoxide. The mixture was stirred at 120°C until gas absorption ceased (ca. 1 h). GLC analysis showed that 3- and 4-phenyl-2-butanone were formed in 65 and 11% yields, respectively, together with styrene (37% based on the bromide charged) as side product. This is, to our knowledge, the first successful catalytic carbonylation of organic halides having β-hydrogens.

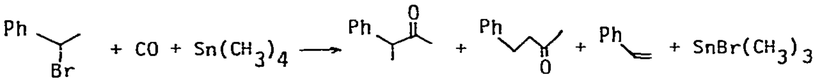
When ethyl α-bromopropionate and α-phenylpropyl bromide were used as

TABLE 1

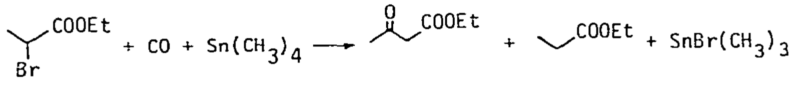
METHYL KETONE SYNTHESIS FROM ORGANIC BROMIDE, CARBON MONOXIDE, AND TETRAMETHYLTIN CATALYZED BY PALLADIUM COMPLEXES[a]

Bromide	$Sn(CH_3)_4$ (mmol)	Catalyst[b] (mmol X 10^2)	Temperature (°C)	Time	Product	Yield (%)	By-product (%)[c]
$PhCHBrCH_3$ (7.5)	3.75	P (1.25)	120	1	$CH_3COCH(CH_3)Ph$ $CH_3COCH_2CH_2Ph$	64.8 11.1	$PhCH{=}CH_2$ (37.1)
$PhCHBrCH_3$ (7.5)	3.75	As (1.25)	120	1	$CH_3COCH(CH_3)Ph$ $CH_3COCH_2CH_2Ph$	101.6[d] 3.6	$PhCH{=}CH_2$ (27.7)
$PhCHBrCH_3$ (1.88)	1.97	As (0.63)	120	2	$CH_3COCH(CH_3)Ph$ $CH_3COCH_2CH_2Ph$	70.4 3.7	$PhCH{=}CH_2$ (14.3)
$PhCHBrCH_3$ (7.5)	3.75[e]	As (3.75)	120	1	$PhCOCH(CH_3)Ph$ $PhCOCH_2CH_2Ph$	43.7 8.0	$PhCH{=}CH_2$ (33.1)
$PhCHBrCH_2CH_3$ (1.88)	1.97	P (1.25)	120	0.6	$CH_3COCH(C_2H_5)Ph$ $CH_3COCH(CH_3)CH_2Ph$ $CH_3COCH_2CH_2CH_2Ph$	17.3 3.2 0.5	$PhCH{=}CHCH_3$ (55.6)
$PhCHBrCH_2CH_3$ (1.88)	1.97	P (1.25)	100	2	$CH_3COCH(C_2H_5)Ph$ $CH_3COCH(CH_3)CH_2Ph$ $CH_3COCH_2CH_2CH_2Ph$	35.5 3.4 0.4	$PhCH{=}CHCH_3$ (50.1)
$PhCHBrCH_2CH_3$ (1.88)	1.97	P (1.25)	80	7	$CH_3COCH(C_2H_5)Ph$ $CH_3COCH(CH_3)CH_2Ph$ $CH_3COCH_2CH_2CH_2Ph$	50.2 1.2 0.0	$PhCH{=}CHCH_3$ (36.3)
$PhCHBrCH_2CH_3$ (1.88)	1.97	As (3.75)	120	0.5	$CH_3COCH(C_2H_5)Ph$ $CH_3COCH(CH_3)CH_2Ph$ $CH_3COCH_2CH_2CH_2Ph$	33.2 1.1 0.1	$PhCH{=}CHCH_3$ (43.4)
$CH_3CHBrCOOC_2H_5$ (3.75)	1.88	P (1.88)	120	1	$CH_3COCH(CH_3)COOC_2H_5$ $CH_3COCH_2CH_2COOC_2H_5$	13.9 0.0	$CH_3CH_2COOC_2H_5$ (25.1)
$CH_3CHBrCOOC_2H_5$ (7.5)	3.75	As (3.75)	120	3	$CH_3COCH(CH_3)COOC_2H_5$ $CH_3COCH_2CH_2COOC_2H_5$	62.2 0.0	$CH_3CH_2COOC_2H_5$ (24.6)

[a] $P(CO)$ = 20 atm (room temperature). [b] P and As stand for $PdCl_2(PPh_3)_2$ and $PdCl_2(AsPh_3)_2$, respectively. [c] Based on the amount of halides charged. [d] A second methyl group of tetramethyltin can, albeit less facilely than the first, be incorporated into methyl ketone synthesis; see ref. 7. [e] $SnPh_4$ was used in place of $Sn(CH_3)_4$.


(1)

substrates, the yield of the corresponding ketone was very low due to the extensive side reactions (reduction, olefin formation, and/or isomeric ketone formation). However, the olefin formation from α-phenylpropyl bromide was suppressed considerably by lowering the reaction temperature (see Table 1), and the corresponding ketone became the major product.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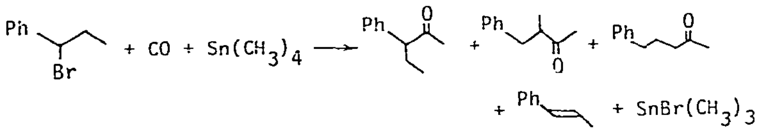

(3)

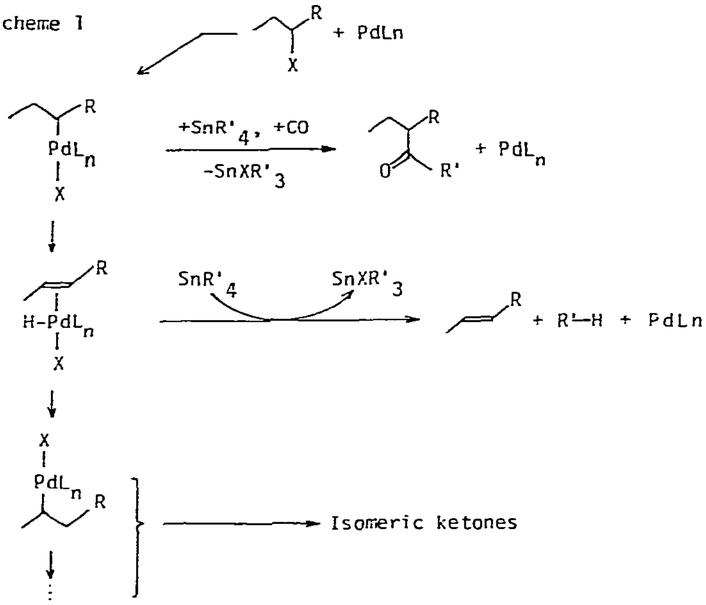
In order to obtain the corresponding ketones selectively in good yields, many other complex catalysts were examined. Despite the somewhat low catalytic activity, $PdCl_2(AsPh_3)_2$ was a better catalyst for selective formation of ketones than was $PdCl_2(PPh_3)_2$. As the data in Table 1 reveal, the yields of ketones are much higher with the $PdCl_2(AsPh_3)_2$ catalyst than with $PdCl_2(PPh_3)_2$. Moreover, higher selectivity to the corresponding ketones in the formation of ketone isomers is observed with the arsine complex than with the phosphine complex.

Although a number of processes are possible as the pathways to give the side products, in view of numerous relevant investigations [8—17], it may be reasonable to consider that those pathways which are initiated by β-hydride elimination after the oxidative addition of a halide are most probable for the formation of isomeric ketones and olefins (Scheme 1). The validity of Scheme 1 is supported by the observation that benzene was formed in the ketonization of α-phenylethyl bromide with tetraphenyltin and that the amount of benzene formed was nearly equivalent to that of styrene.

The results described above seem to indicate that triphenylarine, as compared to triphenylphosphine, facilitates CO insertion which is competitive with β-hydride elimination. The following observations may serve as evidence for this: Carbon monoxide was bubbled into a chloroform-d_3 solution of p-$CH_3OC_6H_4PdI(AsPh_3)_2$ at 0°C for 90 sec in an NMR tube. The gas over the solution was replaced with nitrogen. The NMR spectrum of the resulting solution showed that 93% of the starting p-anisyl complex was converted to the corresponding p-anisoyl complex. On the other hand, only 30% of p-$CH_3OC_6H_4PdI(PPh_3)_2$ was converted to the p-anisoyl complex by the same treatment.

Preliminary carboxylation experiments also showed the superior nature of the triphenylarsine complex catalysts. Treatment of α-phenylethyl bromide with carbon monoxide (20 atm) and methanol in the presence of triethyl-

Scheme 1



(L = PPh_3, $AsPh_3$, and/or CO)

amine with $PdCl_2(AsPh_3)_2$ (0.3%) at 120°C for 4 h gave methyl α- and β-phenylpropionate in 30.1 and 5.2% yield, respectively, together with styrene (15.8%), while the same treatment with $PdCl_2(PPh_3)_2$ gave the α-, β-ester, and styrene in 6.2, 1.0, and 22.3% yield, respectively.

Investigations, including search for better ligands to accelerate CO insertion, are under way.

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