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Palladium Catalyzed Coupling Reaction of α-Bromo Ketones with Hexabutylditin

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Synopsis. Palladium-catalyzed reaction of α-bromo ketones with hexabutylditin in the presence of trimethylsilyl chloride gave enol trimethylsilyl ether in moderate to good yields.

There have been so far known two methods for the preparation of tributyltin enolates (α-tributylstannyl ketones and/or enol tributylstannyl ethers).[1] The one is the reaction of enol acetates with tributyltin methoxide, and the other is the addition of tributyltin hydride to α,β-unsaturated ketones.

$$\mathrm{RHC{=}CHOAc + Bu_3SnOMe \longrightarrow RHC{=}CHOSnBu_3 + AcOMe}$$

$$\mathrm{RHC{=}CH\text{-}COR' + Bu_3SnH \longrightarrow RCH_2CH{=}CR'OSnBu_3}$$

For the preparation of organotin compounds, the coupling reaction between hexabutylditin and organic halides in the presence of palladium complexes is recently developped.[2]

$$\mathrm{RX + Bu_3SnSnBu_3 \xrightarrow{[Pd]} RSnBu_3 + Bu_3SnX}$$

In order to develop another route for preparation of tributyltin enolates, we applied the above coupling reaction to α-bromo ketones.

$$\mathrm{BrCH_2COR + Bu_3SnSnBu_3 \xrightarrow{[Pd]} CH_2{=}CROSnBu_3 + Bu_3SnBr}$$

Initially we carried out the reaction of α-bromoacetophenone with hexabutylditin in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium. However, isolated products were tributyltin bromide and acetophenone. This means that tin enolate was not produced or was not stable enough under the reaction conditions. According to Lutsenko *et al.*[3] addition of trimethylsilyl chloride into tin enolate gave stable enol trimethylsilyl ether in good yield as the result of tin-silicon exchange. Then we tried to convert the tin enolate produced into enol silyl ether, by carring out the reaction in the presence of trimethylsilyl chloride. Results are shown in Table 1.

Table 1. Pd-Catalyzed reaction of α-bromo ketones with hexabutylditin in the presence of trimethylsilyl chloride

$$\underset{12\text{ mmol}}{\mathrm{Bu_3SnSnBu_3}} + \underset{10\text{ mmol}}{\mathrm{R\text{-}Br}} + \underset{12\text{ mmol}}{\mathrm{Me_3SiCl}} \xrightarrow[80\,^{\circ}\mathrm{C},\ 20\,\mathrm{h\ in\ tetralin}\ 10\,\mathrm{cm^3}]{[\mathrm{Pd}]\ 0.1\ \mathrm{mmol}}$$

R-Br	Catalyst[a)]	Product	Yield/%[b)]
$\mathrm{BrCH_2COEt}$	A	$\mathrm{CH_2{=}CEtOSiMe_3}$	69
$\mathrm{BrCH_2COBu^t}$	A	$\mathrm{CH_2{=}CBu^tOSiMe_3}$	81
MeCHBrCOMe	A	$\mathrm{MeCH{=}CMeOSiMe_3}$	77
$\mathrm{Me_2CBrCOMe}$	A	$\mathrm{Me_2C{=}CMeOSiMe_3}$	75
$\mathrm{BrCH_2COPh}$	A	$\mathrm{CH_2{=}CPhOSiMe_3}$	65
$\mathrm{BrCH_2CO_2Et}$	B[c)]	$\mathrm{Me_3SiCH_2CO_2Et}$	79
$\mathrm{MeCHBrCO_2Et}$	B[c)]	$\mathrm{Me_3SiCHMeCO_2Et}$	49
$\mathrm{BrCH_2CN}$	B	$\mathrm{Me_3SiCH_2CN}$	61
$\mathrm{BrCH_2NO_2}$	B	$\mathrm{Me_3SiCH_2NO_2}$	—

a) A: $\mathrm{Pd(PPh_3)_4}$, B: $\mathrm{PdCl_2[P(\mathit{o}\text{-tolyl})_3]_2}$. b) Isolated yield based on R-Br. c) HMPA was used as solvent.

As Table 1 shows, moderate to good yields of enol silyl ethers were obtained. From the reaction of α-bromo carboxylates, α-trimethylsilyl carboxylates were produced, but not ketene silyl acetals, even when the reaction was carried out in the presence of trimethylsilyl iodide.[3] Similarly, from the α-bromoacetonitrile, trimethylsilylacetonitrile was obtained, but (trimethylsilyl)nitromethane could not be obtained from the reaction of bromonitromethane.

The following three possible reaction sequences can be considered for the formation of the enol silyl ether from this reaction system.

The first:

$$\mathrm{2Me_3SiCl + Pd(PPh_3)_4 \longrightarrow Me_3SiSiMe_3 + PdCl_2(PPh_3)_2}\ ^{4)}$$

$$\mathrm{Me_3SiSiMe_3 + BrCH_2COR \xrightarrow{[Pd]} CH_2{=}CROSiMe_3 + Me_3SiBr}\ ^{5)}$$

The second:

$$\mathrm{Bu_3SnSnBu_3 + Me_3SiCl \xrightarrow{[Pd]} Bu_3SnSiMe_3 + Bu_3SnCl}$$

$$\mathrm{Bu_3SnSiMe_3 + BrCH_2COR \xrightarrow{[Pd]} CH_2{=}CROSiMe_3 + Bu_3SnBr}\ ^{6)}$$

The third:

$$\mathrm{Bu_3SnSnBu_3 + BrCH_2COR \xrightarrow{[Pd]} CH_2{=}CROSnBu_3 + Bu_3SnBr}$$

$$\mathrm{CH_2{=}CROSnBu_3 + Me_3SiCl \longrightarrow CH_2{=}CROSiMe_3 + Bu_3SnCl}$$

Since the reaction in the absence of hexabutylditin did not give the enol silyl ether, and the reaction of hexamethyldisilane with α-bromo ketone in the presence of palladium complex did not occur, the first possibility is excluded. The second one is also unlikely, because the reaction of hexabutylditin with trimethylsilyl chloride in the presence of palladium catalyst also did not produce the (trimethylsilyl)tributyltin. Thus, the third one is most plausible, that is, the coupling between hexabutylditin and α-bromo ketone is thought to actually occur, forming the tin enolates. In the absence of trimethylsilyl chloride, the tin enolate seemed to collapse to the corresponding ketone.

Other trial for trapping tin enolates also shows the formation of tin enolates in this reaction, although trapping efficiency was not so high. For example, the palladium-catalyzed reaction of α-bromoacetophenone with hexabutylditin in the presence of benzaldehyde gave 1,3-diphenyl-2-propen -1- one[7] in 30% yields.

Experimental

IR spectra were recorded on a Jasco A-100 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM-360 instrument. GLC analyses were carried out with Ohkura 802 instrument, using columns (1.5 m) packed with 10% Silicone SF-96 and SE-30 on Celite 545.

Materials. α-Bromo ketones and palladium complexes were used reported previously.[6] Ethyl bromoacetate, ethyl 2-bromopropionate, and bromoacetonitrile were commercially available. Bromonitromethane was prepared by the method described in literature.[8]

Reaction Procedure. The mixture of hexabutylditin (12 mmol), bromide (10 mmol), trimethylsilyl chloride (12 mmol), palladium complex (0.1 mmol), and tetralin (10 cm^3) as solvent is heated under argon at 80 °C for 20 h. Products were collected in cold trap by vacuum distillation under room temperature.

Products. All the products were known. Enol trimethylsilyl ethers were reported previously.[6] ^{1}H NMR and IR data using in identification of ethyl trimethylsilylacetate, ethyl 2-(trimethylsilyl)propionate, and trimethylsilylacetonitrile were recorded here.

Ethyl Trimethylsilylacetate; ^{1}H NMR (CCl$_4$) $\delta=0.15$ (s, 9H), 1.24 (t, $J=7$ Hz, 3H), 1.78 (s, 2H), and 4.02 (q, $J=7$ Hz, 2H). IR (neat): 1720 (C=O), 1365, 1245, 1240, 1100, and 850 cm^{-1}.

Ethyl 2-(Trimethylsilyl)propionate; ^{1}H NMR (CCl$_4$) $\delta=0.05$ (s, 9H), 1.20 (t, $J=7$ Hz, 3H), 1.25 (d, $J=7$ Hz, 3H), 1.87 (q, $J=7$ Hz, 1H), and 4.07 (q, $J=7$ Hz, 2H). IR (neat): 1730 (C=O), 1350, 1245, 1235, 1095, and 870 cm^{-1}.

Trimethylsilylacetonitrile; ^{1}H NMR (CCl$_4$) $\delta=0.15$ (s, 9H) and 1.44 (s, 2H). IR (neat): 2220 (CN), 1390, 1255, and 850 cm^{-1}.

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