(α-Ethoxyvinyl)tributyltin; An Efficient Reagent for the Nucleophilic Acetylation of Organic Halides via Palladium Catalysis

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Synopsis. (α-Ethoxyvinyl)tributyltin acts as a masked acetylating agent in the palladium catalyzed reaction with various organic halides, such as aryl bromides, vinyl bromides, benzyl chloride, and allyl chloride, giving, after hydrolysis of the resulting reaction mixture, good yields of the corresponding ketone product.

Several reports of ketone syntheses via cross-coupling of organometallics and organic halides have been reported. Palladium catalyzed reactions of organotin compounds with acid chlorides[1] or with organic halides and carbon monoxide[2] are shown to be useful for the preparation of ketone. Recently, palladium catalyzed reaction of α-methoxyvinylzinc compound prepared in situ with organic halides after hydrolytic treatment was reported for the ketone synthesis.[3] Similar reaction of the corresponding tin compound with acid chlorides catalyzed by palladium was reported for the preparation of α-diketones.[4] α-Diketones were also prepared by palladium catalyzed reaction of acid chlorides with acyltin compounds.[5]

In this note, we report the utility of (α-ethoxyvinyl)-tributyltin as a masked acetylating agent in the reactions with organic halides (not only with acid chlorides, but also with aryl and vinyl bromides, benzyl chloride, and allyl chloride). (Eq. 1)

$$n\text{-Bu}_3\text{SnC(OEt)} = \text{CH}_2 + \text{R-X} \xrightarrow{[\text{Pd}]} \xrightarrow{\text{H}^+} \text{R-COCH}_3 \quad (1)$$

As is shown in Table 1, the catalytic efficiency of this reaction, which proceeds smoothly in the presence of only 1 mol% of the catalyst, may be better than that in the reaction of the zinc reagents, which needs 5 mol% of the catalyst.[3] Both of palladium(0) and palladium(II) catalysts gave almost the same results. This implies that palladium(II) complex was reduced by the tin compound under the reaction conditions. The use of nonpolar solvent is recommendable, although the solvent effect was not large. GLC analysis shows that the reaction with bromobenzene proceeds nearly quantitatively. Substituted acetophenones were obtained in good yields from aryl bromides containing a variety of ring functional groups. With β-bromostyrene, the stereochemistry of the substrate was not retained, in contrast to Hegedus's findings for the organozinc compounds.[3]

Experimental

IR spectra were recorded on Jasco A-100 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM-360 instrument, using tetramethylsilane as an internal standard. 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-Ethoxyvinyl)tributyltin was prepared according to the method described in the literature.[6] Bp.

Table 1. Reaction of (α-Ethoxyvinyl)tributyltin with Organic Halides at 100°C

R-X	Catalyst[a]	Solvent	Yield of R-COMe/%[b]
Ph-Br	None	PhH	0
Ph-Br	A	PhH	(100)
Ph-Br	B	PhH	(100), 80
Ph-Br	C	PhH	(17)
Ph-Br	D	PhH	Trace
Ph-Br	B	DMF	(81)
Ph-Br	B	HMPA	(60)
p-MeC_6H_4-Br	B	PhMe	67
m-MeC_6H_4-Br	B	PhMe	70
o-MeC_6H_4-Br	B	PhMe	78
p-ClC_6H_4-Br	B	PhMe	73
p-$MeOC_6H_4$-Br	B	PhMe	54
p-AcC_6H_4-Br	B	PhMe	89
p-NCC_6H_4-Br	B	PhMe	81
p-$O_2NC_6H_4$-Br	B	PhMe	91
(*E*)PhCH=CH-Br[c]	B	PhMe	63 (E)
(*Z*)PhCH=CH-Br[c]	B	PhMe	73 (E)
$PhCH_2$-Cl[c]	B	PhMe	72
CH_2=$CHCH_2$-Cl[c]	B	PhMe	43
PhCO-Cl	E	PhH	75[d]

a) A: $Pd(PPh_3)_4$, B: $PdCl_2(PPh_3)_2$, C: $PdCl_2[P(o\text{-tolyl})_3]_2$, D: $Pd_2(dba)_3 \cdot CHCl_3$,[e] E: $PhCH_2PdCl(PPh_3)_2$. b) Isolated yield based on the halide, in parenthesis GLC yield of α-ethoxystyrene. c) At 80°C. d) Results shown in Ref. 4. e) dba: dibenzylideneacetone.

106/0.4 mmHg (1 mmHg=133.322 Pa). ^{1}H NMR (C_6D_6) δ=0.7—1.8 (m, 30H), 3.60 (q, J=8Hz, 2H), 4.30 (d, J=2Hz, 1H), and 4.83 (d, J=2Hz, 1H). GC-MS m/z 305 (M^+—Bu, 100). Preparation of halides and palladium complexes were already reported.[7]

Reaction Procedures. A mixture of (α-ethoxyvinyl)-tributyltin (5.5 mmol), halide (5.0 mmol), dichlorobis(triphenylphosphine)palladium (0.05 mmol), and toluene (2 cm^3) was heated under argon at 100 °C for 20 h. After hydrolysis of the reaction mixture with 5% hydrochloric acid, the organic layer was extracted with diethyl ether, and dried over sodium sulfate. After evaporation of the solvent, column chromatography of the residue (silica gel; cyclohexane followed by diethyl ether) provided the ketones in the ethereal eluents and the product was isolated by distillation under reduced pressure.

Products. All the products were known and their structures were determined by comparison of their spectroscopic data with the reported values.[3,8,9]

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