Palladium-catalyzed Reaction of Stannyl Sulfide with Aryl Bromide. Preparation of Aryl Sulfide

Masanori KOSUGI,* Toshimi OGATA, Masahiro TERADA, Hiroshi SANO, and Toshihiko MIGITA*
Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Gunma 376
(Received August 5, 1985)

Synopsis. Tributylstannyl alkyl or aryl sulfide and bis(tributylstannyl) sulfide were found to be useful to prepare aryl sulfides in good yields under the usual conditions of the palladium-catalyzed reaction with aryl bromides.

Versatility of organotin reagents can be found in that organotin compounds having either carbon–tin bond[1] or heteroatom–tin bond can be utilized in palladium-catalyzed cross-coupling with organic halides. Thus, silylstannane,[2] distannane,[3] and aminostannane[4] transfer silyl, stannyl, and amino groups to aryl halides, respectively. However, palladium-catalyzed alkoxylation or acyloxylation of aryl halides by using the alkoxy or acyloxy tin compounds is not attained so far. In contrast, stannyl sulfide, an analogue of stannyl alkoxide, was found to undergo the cross-coupling with aryl bromides.[6]

In this note, we report the palladium-catalyzed reaction of stannyl sulfides with aryl bromides.

$$n\text{-Bu}_3\text{SnSR} + \text{ArBr} \xrightarrow{[\text{Pd}]} \text{ArSR} + n\text{-Bu}_3\text{SnBr}$$

Previously we reported that aryl phenyl or aryl alkyl sulfides were formed by the reaction of sodium benzenethiolate or alkanethiolate with aryl iodides or bromides, catalyzed by palladium.[5] The present method is an alternative one without any use of strong base and is applied to aryl bromides bearing wider variety of substituents. Results are summarized in Table 1.

The reaction took place with either butylthio or phenylthio tin compounds and gave the sulfides in good yields regardless of the nature of functional groups in substrates. With mesityl bromide, the yield was rather low probably due to steric hindrance. As the yield did not depend on the solvent polarity, we chose aromatic hydrocarbon for the convenience of its removal in workup processes.

The reaction of bis(tributylstannyl) sulfide was exemplified for the preparation of symmetrical sulfide as shown in Table 2, although the palladium-catalyzed reaction of aryl iodides or vinyl bromides with bis(triethylstannyl) sulfide has appeared in a recent review of Beletskaya[6] without any reference cited. The reaction was carried out under similar conditions to those shown in Table 1. The reaction gave the sulfide in moderate yields except with aryl bromides having ortho substituents. A similar situation was also observed in the reaction with vinyl bromides, showing that steric hindrance might be an important factor in these reactions. Trials for the preparation of unsymmetrical sulfides by using a mixture of two bromides were failed.

Experimental

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

Materials. Tributylstannyl butyl and phenyl sulfide were prepared by treating the corresponding thiols with tributyltin oxide in the presence of base (sodium ethoxide).[7] Bis(tributylstannyl) sulfide was prepared by the reaction of tributyltin oxide with thiourea.[7] Palladium complex and halide were already reported.[1b]

Reaction Procedures. A mixture of stannyl sulfide (1.3 mmol), halide (1.0 or 2.0 mmol), tetrakis(triphenylphosphine)palladium (1 mol%), and toluene or xylene (1 cm^3) was heated under argon at 120 °C for 20 h. After the reaction mixture was washed with aqueous potassium fluoride and filtered to remove tributyltin fluoride, the organic layer was extracted with ether and dried over magnesium sulfate. The product was distilled by Kugelrohr.

Products. Most of the products were known and their structures were identified by IR and ^{1}H NMR spectra.

Di-p-tolyl Sulfide: ^{1}H NMR (CCl_4) δ=2.29 (s, 6H) and 6.8—7.3 (m, 8H). Found: C, 78.05; H, 6.73%. Calcd for $C_{14}H_{14}S$: C, 78.46; H, 6.58%.

Bis(p-chlorophenyl) Sulfide: Found: C, 56.94; H, 3.19%. Calcd for $C_{12}H_8Cl_2S$: C, 56.49; H, 3.16%.

Bis(p-acetylphenyl) Sulfide: IR (CCl_4) 1270 and 1690 cm^{-1} (C=O). ^{1}H NMR (CCl_4) δ=2.50 (s, 6H) and 7.34 and 7.55 (ABq, J=9Hz, 8H). Found: C, 71.19; H, 5.23%. Calcd for $C_{14}H_{14}O_2S$: C, 71.09; H, 5.22%.

Bis(p-cyanophenyl) Sulfide: IR (CCl_4): 2230 cm^{-1} (CN). ^{1}H

TABLE 1. REACTION OF TRIBUTYLSTANNYL BUTYL OR PHENYL SULFIDE WITH ARYL BROMIDES

$$\text{Bu}^n_3\text{SnSR}^1 + \text{X-C}_6\text{H}_4\text{Br} \xrightarrow{[\text{Pd}]^{a)}} \text{X-C}_6\text{H}_4\text{SR}^1 + \text{Bu}^n_3\text{SnBr}$$

R^1	X	Yield of $ArSR^1$/%[b]	R^1	X	Yield of $ArSR^1$/%[b]
Bu^n	H	86	Ph	*p*-Cl	74
Ph	H	(83)	Ph	*o*-Cl	73
Ph	*p*-Me	(76)	Ph	*p*-MeCO	67
Ph	*o*-Me	(67)	Ph	*p*-CN	72
Ph	*p*-MeO	100	Ph	*p*-NO_2	52
Ph	*o*-MeO	66	Ph	2,4,6-Me_3	34

a) $Pd(PPh_3)_4$, b) GLC yields based on the bromide, in parentheses isolated yields.

Table 2. Reaction of bis(tributylstannyl) sulfide with aryl or vinyl bromides

$Bu^n_3SnSSnBu^n_3 + 2R\text{-}Br \xrightarrow{[Pd]^{a)}} R\text{-}S\text{-}R + 2Bu^n_3SnBr$

R-Br	Yield of RSR/%[b]	R-Br	Yield of RSR/%[b]
C_6H_5-	75	*p*-$MeCOC_6H_4$-	52
p-MeC_6H_4-	23	*p*-NCC_6H_4-	57
m-MeC_6H_4-	50	*p*-$O_2NC_6H_4$-	44
p-MeC_6H_4-	60	2,4,6-$Me_3C_6H_2$-	3[c]
p-$MeOC_6H_4$-	62	(E) PhCH=CH-	77
m-ClC_6H_4-	60	Me_2C=CH-	25
p-ClC_6H_4-	86	Me_2C=CMe-	0

a) $Pd(PPh_3)_4$, b) Isolated yields based on the bromide, c) GLC yield.

NMR (CCl_4) δ=7.32 and 7.55 (ABq, J=8Hz). Found: C, 71.56; H, 3.54; N, 11.72%. Calcd for $C_{14}H_8N_2S$: C, 71.16; H, 3.41; N, 11.86%.

Bis(p-*nitrophenyl*) *Sulfide*: IR (CCl_4) 1350 and 1515 cm^{-1} (NO_2). ^1H NMR (CCl_4) δ=7.63 and 8.07 (ABq, J=9Hz). Found: C, 52.32; H, 2.86; N. 10.19%. Calcd for $C_{12}H_8N_2O_4S$: C, 52.17; H, 2.92; N, 10.14%.

The gift of tributyltin oxide by Kohriyama Kasei Co. is gratefully acknowledged.

References

1) a) M. Kosugi, K. Sasazawa, Y. Shimizu, and T. Migita, *Chem. Lett.*, **1977**, 301; b) M. Kosugi, I. Hagiwara, T. Sumiya, and T. Migita, *Bull. Chem. Soc. Jpn.*, **57**, 242 (1984); c). J. W. Labadie, D. Tueting, and J. K. Stille, *J. Org. Chem.*, **48**, 4634 (1983).

2) H. Azizian, C. Eaborn, and A. Pidcock, *J. Organometal. Chem.*, **215**, 49 (1981).

3) M. Kosugi, T. Ohya, and T. Migita, *Bull. Chem. Soc. Jpn.*, **56**, 3855 (1983).

4) M. Kosugi, M. Kameyama, and T. Migita, *Chem. Lett.*, **1983**, 927.

5) T. Migita, T. Shimizu, Y. Asami, J. Shiobara, Y. Kato, and M. Kosugi, *Bull. Chem. Soc. Jpn.*, **53**, 1385 (1980).

6) I. P. Beletskaya, *J. Organometal. Chem.*, **250**, 551 (1983).

7) A. G. Davies and P. J. Smith, "Comprehensive Organometallic Chemistry," ed by Sir G. Wilkinson, Vol. 2, Pergamon Press (1982) p. 604.