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### Palladium-Catalysed Coupling of Organotinulfides with Heteroaromatic Halides

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## PALLADIUM-CATALYSED COUPLING OF ORGANOTINSULFIDES WITH HETEROAROMATIC HALIDES.

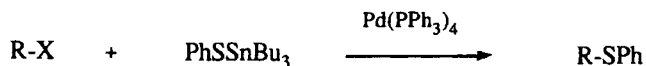
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**Abstract :** The palladium-catalysed coupling of 2- or 3-bromopyridine, 5-bromo or 2- chloro pyrimidine and 5-iodo-1,3-dibenzyluracil with phenyl tributyltin sulfide gave the corresponding heterocyclic phenyl sulfide in good yield.

The coupling of organostannanes with aromatic halides under the influence of a palladium catalyst represents a versatile method for carbon-carbon bond formation.<sup>2</sup> Organostannanes have been coupled to 5-halopyrimidines<sup>3</sup> and 5-iodouracil<sup>4</sup> previously to effect the elaboration of the heterocyclic compound with a carbon side chain. We have previously prepared modified uridine nucleosides by a palladium-catalysed coupling of organostannanes with suitably protected 5-iodouridine and 5-iodo-2'-deoxyuridine.<sup>5</sup> We wished to extend this methodology to thiostannanes with the view to preparing 5-thiouracil derivatives.

As a model system the coupling of phenyl tributyltin sulfide **1** with a variety of haloheterocyclic compounds was investigated .



2-Bromo and 3-bromopyridine, 5-bromo and 2-chloropyrimidine and 5-iodo-1,3-dibenzyluracil **2** all underwent coupling with **1** in the presence of 10% Pd(PPh<sub>3</sub>)<sub>4</sub> in toluene at 100°C and gave good yields of the expected phenylsulfide derivatives ( Table 1 ). In addition, the coupling of ethyl tributyltin sulfide with **2** was undertaken and also gave the expected ethylthio coupled product in good yield.

Since tributyltin cyanide **3** had been shown previously to couple with iodopurine nucleosides<sup>6</sup> the reaction of **3** with **2** was also briefly investigated and the 5-cyanouracil **4** was isolated in 70% yield.

TABLE I Products and Yields from Coupling Reactions

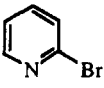
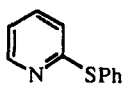
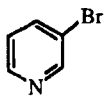
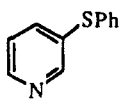
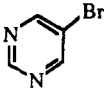
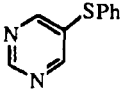
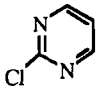
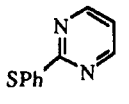
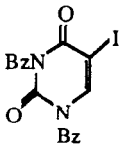
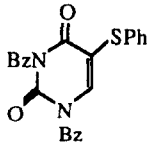
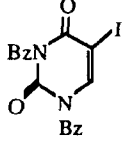
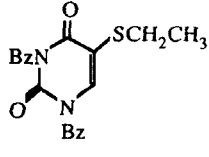


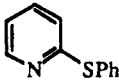
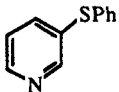
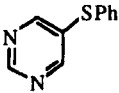
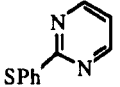
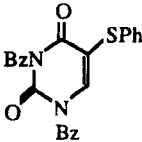
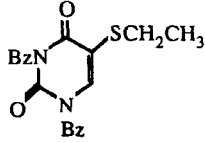

HALIDE	PRODUCT	YIELD %	FORMULA	MOLECULAR WEIGHT	
				Found	Calculated
		85	$C_{11}H_9NS$	187.0454	187.0456
		87	$C_{11}H_9NS$	187.0463	187.0456
		94	$C_{10}H_8N_2S$	188.0407	188.0408
		95	$C_{10}H_8N_2S$	188.0417	188.0408
		89	$C_{24}H_{20}O_2N_2S$	400.1230	400.1245
		71	$C_{20}H_{20}O_2N_2S$	352.1254	352.1245
		70	$C_{19}H_{15}N_3O_2$	317.1157	317.1164

TABLE 2.  $^1\text{H}$  NMR Data for Coupled Products

PRODUCT	$^1\text{H}$ NMR ( $\text{CDCl}_3$ / TMS ) $\delta$ ppm
	6.87 ( dt,0.9 and 8.2Hz,H3 ), 7.06 ( ddd,0.9,4.9 and 7.3Hz,H5 ), 7.40-7.50 ( m,Ar ), 7.61 ( m,H4 ), 8.42 ( ddd,0.8,1.9 and 4.9Hz,H6 )
	7.21 ( dd,4.3 and 8.1Hz,H5 ), 7.4-7.5 ( m,Ar ), 7.59 ( m,H4 ), 8.45 ( d,4.0Hz,H6 ), 8.55 ( s,H2 )
	7.4-7.5 ( m,Ar ), 8.59 ( s,H6 ), 9.03 ( s,H2 )
	6.95 ( t,4.9Hz,H5 ), 7.4-7.6 ( m,Ar ), 8.47 ( d,4.9Hz,H4and6 )
	4.92 ( s,CH <sub>2</sub> ), 5.15 ( s,CH <sub>2</sub> ), 7.2-7.5 ( m,Ar ), 7.51 ( s,H6 )
	1.17 ( t,7.4Hz,CH <sub>3</sub> ), 2.76 ( q,7.4Hz,CH <sub>2</sub> ), 4.92 ( s,CH <sub>2</sub> ), 5.17 ( s,CH <sub>2</sub> ), 7.3-7.5 ( m,Ar ), 7.46 ( s,H6 )
	4.93 ( s,CH <sub>2</sub> ), 5.20 ( s,CH <sub>2</sub> ), 7.3-7.5 ( m,Ar ), 7.58 ( s,H6 )

### Experimental.

Organostannanes were obtained from commercial sources and were used as obtained. The palladium catalyst was prepared according to a literature procedure.<sup>7</sup> 5-Iodo-1,3-dibenzyluracil was prepared according to reference 8.

### General Procedure.

To degassed toluene ( 10 mL ) was added Pd(PPh<sub>3</sub>)<sub>4</sub> ( 0.05mmol ), the haloheterocyclic compound ( 0.5mmol ) and the appropriate organostannane ( 0.55mmol ). The mixture was heated under nitrogen at 100°C for 24 hours. The toluene was removed under vacuum and the residue dissolved in a minimum volume of chloroform and applied to a silica gel column. The product was eluted with ethyl acetate / petroleum ether ( 1: 2 volume ). The yields and spectroscopic data for the compounds are shown in Tables 1 and 2.

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