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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.[2] Organostannanes have been coupled to 5-halopyrimidines[3] and 5-iodouracil[4] 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.[5] 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 .

$$\text{R-X} \quad + \quad \text{PhSSnBu}_3 \xrightarrow{\text{Pd(PPh}_3)_4} \text{R-SPh}$$

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% $Pd(PPh_3)_4$ 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 tributytin cyanide **3** had been shown previously to couple with iodopurine nucleosides[6] the reaction of **3** with **2** was also briefly investigated and the 5-cyanouracil **4** was isolated in 70% yield.

TABLE 1 Products and Yields from Coupling Reactions

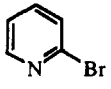
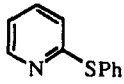
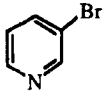
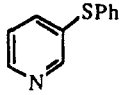
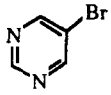
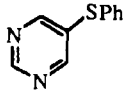
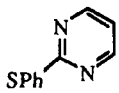
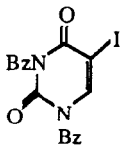
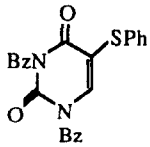
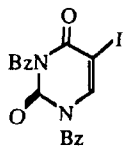
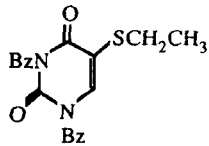
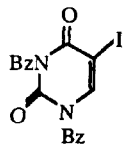
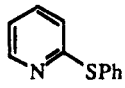
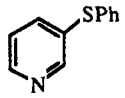
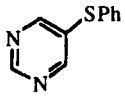
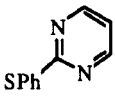
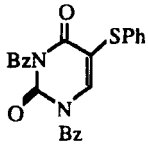
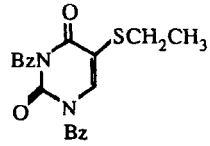
HALIDE	PRODUCT	YIELD %	FORMULA	MOLECULAR WEIGHT	
				Found	Calculated
		85	$C_{11}H_9NS$	187.0454	187.0456
		87	$C_{11}H_9NS$	187.0463	187.0456
		94	$C_{10}H_8N_2S$	188.0407	188.0408
		95	$C_{10}H_8N_2S$	188.0417	188.0408
		89	$C_{24}H_{20}O_2N_2S$	400.1230	400.1245
		71	$C_{20}H_{20}O_2N_2S$	352.1254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

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

PRODUCT	^{1}H NMR ($CDCl_3$ / TMS) δ 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_2), 5.15 (s,CH_2), 7.2-7.5 (m,Ar), 7.51 (s,H6)
	1.17 (t,7.4Hz,CH_3), 2.76 (q,7.4Hz,CH_2), 4.92 (s,CH_2), 5.17 (s,CH_2), 7.3-7.5 (m,Ar), 7.46 (s,H6)
	4.93 (s,CH_2), 5.20 (s,CH_2), 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 .[7] 5-Iodo-1,3-dibenzyluracil was prepared according to reference 8.

General Procedure.

To degassed toluene (10 mL) was added $Pd(PPh_3)_4$ (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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