REACTION OF ACTIVATED ARYL IODIDES WITH Bu_6Sn_2, CATALYZED BY FLUORIDE ION AND $NiBr_2$

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A convenient method for synthesizing $ArSnR_3$ compounds is the cross-combination reaction of ArI with R_6Sn_2, catalyzed by Pd complexes [1]. We showed that in the case of activated ArI (I), this reaction is carried out in hexametapol (HMPT) at 135°C, without a catalyst.

$$\underset{(Ia-c)}{ArI} + Bu_6Sn_2 \rightarrow \underset{(IIa-c)}{ArSnR_3} + R_3SnI \qquad (I)$$

$$Ar = 4\text{-}NO_2C_6H_4\ (a),\ 4\text{-}MeOCOC_6H_4\ (b),\ 4\text{-}ClC_6H_4\ (c)$$

However, on transition from (Ia) to (Ib, c) the rate of the reaction decreases, and (IIb, c) cannot be obtained in a good yield. Phenyl iodide does not react with Bu_6Sn_2. Listed are compounds (I), times of reaction in h, conversion of (I), and yield of (II) in %: (Ia) 7, 100, 73; (Ib), 7, 31, 10; (Ic), 17, 49, 26.

With $NiBr_2$ (10 mole%) as catalyst, the rate of the reaction increased, and compounds (II) were obtained in good yields (listed are compounds (II), times of reaction in h, yield of (II) in %): (IIa), 3, 72; (IIb), 7, 72; (IIc), 17, 92. Phenyl iodide practically does not react with Bu_6Sn_2 under these conditions. The Ni compounds were first used as catalysts in the cross-combination reaction of the organotin compounds. The catalytic effect of $NiBr_2$ is probably due to the transformation of (I) into a more reactive ArNiI complex (the ligands are omitted).

An entirely different approach to reaction (I) consists in the activation of Bu_6Sn_2 as a nucleophile by a fluoride ion. In the presence of 1.1 equivalent of Bu_4NF/SiO_2, the reaction of (Ib) is completed already after 40 min: 65% of (IIb), 19% $PhCO_2Me$ are obtained. By activating distannane by the F^- ion, the Mesenheimer complex $[TNB \cdot Me_3Sn]^-K^+$ (III) (TNB — 1,3,5-trinitrobenzene) was also obtained by the reaction of Me_6Sn_2 with TNB in the presence of KF—18-crown-6-ether system in DMSO at 20°C. The spectral characteristics of (III) are similar to those of a complex obtained previously by the reaction of TNB with Me_2SnK [2]. UV spectrum (in DMSO): λ_{max_1} 438 nm, λ_{max_2} 500 nm $\varepsilon_1/\varepsilon_2 = 1.5$; PMR spectrum (in DMSO, δ, ppm): 8.3 s (2H), 6.2 s (1H), 0.22 s (9H). In the absence of F^-, (III) is formed in trace amounts only.

LITERATURE CITED

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