

Organo-selenium compounds

S 0130

24- 187

A Facile One-Pot Preparation of Organoselanyltrifluoroborates from Dihalobenzenes and Their Cross-Coupling Reaction. — A facile multicomponent reaction of dihalobenzenes like (I) with selenium powder and electrophilic halides (II) is presented, followed by one-pot construction of the trifluoroborate functionality to afford potassium organylselanylphenyltrifluoroborates (III) and (VII) in good yields. The reaction proceeds with a wide variety of electrophiles. The presence of strongly electron-withdrawing substituents like nitro or cyano at the benzyl halides, however, requires a sequential construction of the selanylphenyltrifluoroborates [cf. (X)]. Pd-catalyzed cross coupling reaction of the trifluoroborates with aryl and alkenyl bromides (IV) proceeds smoothly [cf. (V), (VIII)]. — (AHN, H. R.; CHO, Y. A.; KIM, D.-S.; CHIN, J.; GYOUNG, Y.-S.; LEE, S.; KANG, H.; HAM*, J.; Org. Lett. I1 (2009) 2, 361-364; Korea Inst. Sci. Technol., Gangneung 210, S. Korea; Eng.) — Mischke

Br
$$\frac{1. \text{ Ar. Br (II), A)}}{2. \text{ B)}}$$
 Ar. Se $\frac{K^+}{BF_3^-}$ IIIb $\frac{R^1 - Br (IV)}{C}$ Tol. Se $\frac{K^+}{BF_3^-}$ IIIb $\frac{R^1 - Br (IV)}{C}$ Ar. $\frac{R^1 - Br (IV)}{C}$ Tol. Se $\frac{R^1}{BF_3^-}$ IIIb $\frac{R^1 - Br (IV)}{C}$ Ar. $\frac{R^1 - Br (IV)}{C}$ Ar

B): 1 equiv. BuLi, $B(0-iPr)_3$, $-78->-10^{\circ}C$

C): microwaves (80 W), K₂CO₃, Pd(PPh₃)₄ (cat.), 20% aq. dioxane, 130°C, [20 min]

$$I = \frac{1. R^{2}-X \text{ (VI), A)}}{2. B} \xrightarrow{R^{2}-Se} K^{+} \text{ VIIa,b} \xrightarrow{(IVa)} C$$

$$VII \qquad VIII$$

$$a R^{2}: -Me; X: -I \qquad 91\% \qquad a 61\% \qquad b 77\% \qquad c R^{2}: -Mom; X: -CI \qquad 76\% \qquad b 77\% \qquad c R^{2}: -CH_{2}-CH_{2}; X: -Br \qquad 78\% \qquad d R^{2}: -CH_{2}-Cy; X: -Br \qquad 88\%$$

$$1. 2 \text{ equiv. tBuLi, THF, pentane, } -78^{\circ}C$$

$$2. Se, -78->0^{\circ}C$$

$$3. 2 \text{ equiv. tBuLi, } -78^{\circ}C$$

$$4. B(O-iPr)_{3}, -78->-30^{\circ}C$$

$$5. O_{2}N \xrightarrow{Br} (IX), +25^{\circ}C$$

$$6. 1 N \text{ ag. KHF}_{2}$$

$$X 77\%$$