

Transmetalation of Pentafluorophenylmercury Derivatives with Organylmagnesium Bromides

V. V. Bardin^{a*}

^a N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
 ul. Akademika Lavrentieva 9, Novosibirsk, 630090 Russia

*e-mail: bardin@nioch.nsc.ru

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Abstract—The reactions of pentafluorophenylmercury derivatives with organomagnesium compounds have been studied. The interaction of pentafluorophenylmercury chloride with RMgBr (R = Et, Ph) has afforded diphenyl- and diethylmercury or phenylmercury chloride, besides the expected product (C₆F₅HgR). The results have been explained by the transmetalation of C₆F₅HgR with the Grignard reagent, followed by the reaction of the resulting C₆F₅MgX (X = Br, C₆F₅) with pentafluorophenylmercury chloride. Transmetalation of (C₆F₅)₂Hg with organylmagnesium bromides has led to the formation of C₆F₅MgX and R₂Hg.

Keywords: transmetalation, bis(pentafluorophenyl)mercury, diethylmercury, diphenylmercury, ethylmagnesium bromide, phenylmagnesium bromide

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One of the approaches to the synthesis of asymmetrical organyl mercury derivatives R¹HgR² is a halogen (X) substitution in the R¹HgX derivatives under the action of a nucleophile R²MgX. For example, the interaction of isobutylmercury chloride with RMgBr (R = Alk, CH=CH₂, C≡CH, Ph, C₆Cl₅) [1] has afforded a series of asymmetrical derivatives (CH₃)₂CHCH₂HgR (yield 50–80%) and the R¹HgR² compounds (R¹, R² = Alk, Ar). The latter ones have been prepared via two ways: the reactions of R¹MgBr with R²HgBr or R¹HgBr with R²MgBr [2]. Polyfluorinated aromatic derivatives of mercury Ar_FHgR have been prepared by the reaction of RHgX (R = Me, Et, Ph) with nucleophiles Ar_FM (Ar_F = C₆F₅, 2,3,4,5-C₆F₄H; M = Li, MgX) [3–6]. This method is not advantageous due to low nucleophilicity of Ar_FM and their thermal instability.

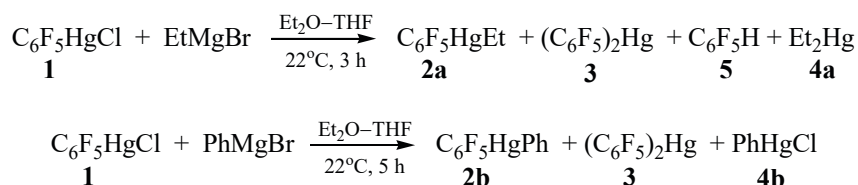
In this study, we attempted an alternative approach to the synthesis of mercury derivatives Ar_FHgR exemplified

by the reaction of pentafluorophenylmercury chloride **1** with organomagnesium compounds. The reaction with EtMgBr, besides the expected pentafluorophenyl(ethyl)mercury **2a**, unexpectedly led to the formation of a mixture of di(pentafluorophenyl)mercury **3**, diethylmercury **4a**, and pentafluorobenzene **5** (Scheme 1). A similar mixture was obtained in the reaction of compound **1** with PhMgBr.

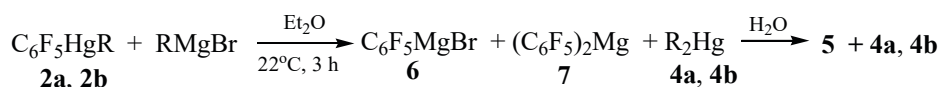
The increase in the reaction duration from 3 to 19 h (R = Et) did not lead to the conversion of pentafluorophenyl(ethyl)mercury **2a** into compounds **3** and **4a**, which ruled out the formation of the latter via symmetrization of the arylalkylmercury **2a**. Likely, transmetalation of C₆F₅HgR occurred under the action of the Grignard reagent with the formation of C₆F₅MgX, which was not observed in the case of the above-mentioned arylmercury derivatives [1, 2].

Indeed, the interaction of C₆F₅HgEt with EtMgBr led to the formation of pentafluorophenylmagnesium bromide **6**,

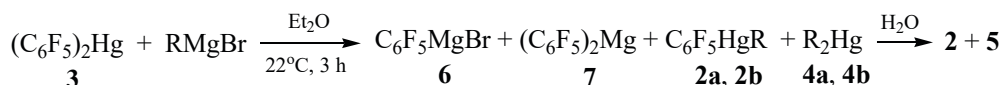
Scheme 1.



Scheme 2.

R = Et (**a**), Ph (**b**).

Scheme 3.

R = Et (**a**), Ph (**b**).

bis(pentafluorophenyl)magnesium **7**, and diethylmercury (Scheme 2). Similarly, the reaction of $\text{C}_6\text{F}_5\text{HgPh}$ with PhMgBr gave compounds **6**, **7**, and diphenylmercury **4b** (^{19}F and ^{199}Hg NMR). Hydrolysis of the reaction mixture led to conversion of products **6** and **7** into pentafluorobenzene (Scheme 2).

Interestingly, the treatment of an equimolar mixture of compounds **2a** and **2b** with 1.3 eq. of EtMgBr in ether resulted in complete conversion of $\text{C}_6\text{F}_5\text{HgPh}$, while the amount of $\text{C}_6\text{F}_5\text{HgEt}$ remaining unchanged (^{19}F NMR). That fact evidenced significant effect of the substituent R in the starting $\text{C}_6\text{F}_5\text{HgR}$ on the transmetalation rate. Nevertheless, di(pentafluorophenyl)mercury, as compounds **2a**, **2b**, underwent to transmetalation under the action of RMgBr . The reaction occurred within 3 h and led to the formation of magnesium derivatives **6** and **7** as well as the corresponding organomercury compounds **2a**, **4a** and **2b**, **4b** (Scheme 3).

More comprehensive analysis of the reasons for the difference in the reactivity of perfluorinated organomercury compounds towards the Grignard reagents from that of the non-fluorinated analogs demands additional experiments involving polyfluorinated derivatives of alkenyl- and alkynylmercury.

In summary, in contrast to the known method of preparation of asymmetrical mercury compounds ArHgR and their fluorinated analogs $\text{Ar}_\text{F}\text{HgR}$ from ArM ($\text{Ar}_\text{F}\text{M}$) and RHgX , the alternative approach based on the interaction of organomagnesium nucleophiles RMgBr with pentafluorophenylmercury derivatives gave a mixture of symmetrical and asymmetrical products $\text{C}_6\text{F}_5\text{HgR}$, $(\text{C}_6\text{F}_5)_2\text{Hg}$, and R_2Hg ($\text{R} = \text{Alk}, \text{Ar}$). The reaction involved perfluoromagnesium compounds formed via transmetalation of perfluoroarylmercury compounds with the Grignard reagents.

EXPERIMENTAL

$(\text{C}_6\text{F}_5)_2\text{Hg}$, $\text{C}_6\text{F}_5\text{HgPh}$ [**3**], $\text{C}_6\text{F}_5\text{HgCl}$, and $\text{C}_6\text{F}_5\text{HgEt}$ [**6**] were synthesized by the known procedures. The yield of the fluorinated products was determined by ^{19}F NMR spectroscopy with internal reference C_6F_6 or $\text{C}_6\text{H}_5\text{F}$. The yield of the organomercury products was determined by the ^{199}Hg NMR spectroscopy by comparison of the intensity of the considered signal with that of pentafluorophenylmercury compound, the content of which was determined from the ^{19}F NMR spectroscopy. The NMR data for compounds **6** and **7** [**7**], **5** [**8**, **9**] (^{19}F), and **4a–4c** [**10**] (^{199}Hg) coincided with the reference ones. The operations were performed under dry argon atmosphere.

NMR spectra were recorded using Bruker Avance 300 (^{19}F , 282.40 MHz) and Avance 600 (^{199}Hg , 107.51 MHz) instruments.

Reaction of pentafluorophenylmercury 1 with RMgBr . *a. R = Et.* 0.54 M. solution of EtMgBr in diethyl ether (1.0 mL, 0.54 mmol) was added to a stirred solution of compound **1** (175 mg, 0.43 mmol) in 2.5 mL of THF. The obtained solution was kept at 22°C during 5 h. A mixture of compounds **2a** (0.19 mmol), **3** (0.16 mmol), diethylmercury (0.14 mmol), and pentafluorobenzene (0.04 mmol) was obtained (^{19}F and ^{199}Hg NMR data).

b. R = Ph. The reaction was performed similarly using 182 mg (0.45 mmol) of compound **1** in 1 mL of THF and 0.51 M. solution of PhMgBr in diethyl ether (1.0 mL, 0.51 mmol); reaction duration 3 h. A mixture of compounds **2b** (0.31 mmol), **3** (0.09 mmol), and **4c** (0.10 mmol) was obtained (^{19}F and ^{199}Hg NMR data).

Reaction of pentafluorophenyl(ethyl)mercury 2a with EtMgBr . 0.54 M. solution of EtMgBr in diethyl ether (1.2 mL, 0.64 mmol) was added to a stirred solution of compound **2a** (225 mg, 0.56 mmol) in 2 mL of

diethyl ether. The obtained solution was kept at 22°C during 5 h. A mixture of compounds **2a** (0.09 mmol), **6** (0.34 mmol), **7** (0.10 mmol), and **4a** (0.40 mmol) was obtained (^{19}F and ^{199}Hg NMR data). 1 mL of 5% HCl was added to the obtained solution, the organic phase was separated and dried over MgSO_4 . The solution contained $\text{C}_6\text{F}_5\text{HgEt}$ (0.09 mmol) and $\text{C}_6\text{F}_5\text{H}$ (0.33 mmol) (^{19}F NMR data).

Reaction of pentafluorophenyl(phenyl)mercury 2b with PhMgBr. 0.51 M. solution of PhMgBr in diethyl ether (1 mL, 0.51 mmol) was added to a stirred solution of compound **2b** (213 mg, 0.47 mmol) in 1.5 mL of diethyl ether. The obtained solution was kept at 22°C during 3 h. A mixture of compounds **2b** (0.18 mmol), **6** (0.19 mmol), **7** (0.09 mmol), and **4b** (0.52 mmol) was obtained (^{19}F and ^{199}Hg NMR data). 1 mL of 5% HCl was added to the obtained solution, the organic phase was separated and dried over MgSO_4 . The solution contained $\text{C}_6\text{F}_5\text{HgPh}$ (0.16 mmol) and $\text{C}_6\text{F}_5\text{H}$ (0.28 mmol) (^{19}F NMR data).

Competing reactions of pentafluorophenyl(ethyl)mercury 2a and pentafluorophenyl(phenyl)mercury 2b with EtMgBr. 0.54 M. solution of EtMgBr in diethyl ether (1.0 mL, 0.54 mmol) was added to a stirred solution of compounds **2a** (175 mg, 0.43 mmol) and **2b** (177 mg, 0.40 mmol) in 2.5 mL of diethyl ether. The obtained mixture was kept at 22°C during 18 h. A mixture of compounds **2a**, **6**, **7**, and **5** (10 : 5 : 1 : 1) was obtained (^{19}F NMR data). 1 mL of 5% HCl was added to the obtained solution, the organic phase was separated and dried over MgSO_4 . The solution contained $\text{C}_6\text{F}_5\text{HgEt}$ (0.40 mmol) and pentafluorobenzene (0.32 mmol) (^{19}F NMR data).

Reaction of bis(pentafluorophenyl)mercury 3 with RMgBr. *a. R = Et.* The reaction between compound **3** (146 mg, 0.27 mmol) in 1 mL of diethyl ether and 0.54 M. solution of EtMgBr in diethyl ether (1.0 mL, 0.54 mmol) was performed similarly during 3 h. A mixture of compounds **2a** (0.08 mmol), **6** (0.57 mmol), **7** (0.15 mmol), and **4a** (0.35 mmol) was obtained. Compounds **2a** (0.08 mmol) and **5** (0.42 mmol) were obtained upon hydrolysis (^{19}F NMR data). The presence of compound **4a** was not verified.

b. R = Ph. The reaction was performed similarly using a solution of 144 mg (0.27 mmol) of compound **3** in 1 mL of diethyl ether and 0.51 M. solution of PhMgBr in diethyl ether (1.0 mL, 0.51 mmol); reaction duration 3 h. A mixture of compounds **2b** (0.14 mmol), **6** (0.20 mmol), **7** (0.06 mmol), and **4b** (0.09 mmol) was obtained. Upon keeping the mixture during 48 h and hydrolysis, the products contained compounds **2b** (0.14 mmol) and **5** (0.27 mmol) (^{19}F NMR data). The presence of compound **4a** was not verified.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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