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Transmetalation of Pentafluorophenylmercury Derivatives with Organylmagnesium Bromides

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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 (C_6F_5HgR). The results have been explained by the transmetalation of C_6F_5HgR with the Grignard reagent, followed by the reaction of the resulting C_6F_5MgX (X = Br, C_6F_5) with pentafluorophenylmercury chloride. Transmetalation of $(C_6F_5)_2Hg$ with organylmagnesium bromides has led to the formation of C_6F_5MgX and R_2Hg.

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 R^1HgR^2 is a halogen (X) substitution in the R^1HgX derivatives under the action of a nucleophile R^2MgX. For example, the interaction of isobutylmercury chloride with RMgBr (R = Alk, $CH=CH_2$, $C\equiv CH$, Ph, C_6Cl_5) [1] has afforded a series of asymmetrical derivatives $(CH_3)_2CHCH_2HgR$ (yield 50–80%) and the R^1HgR^2 compounds (R^1, R^2 = Alk, Ar). The latter ones have been prepared via two ways: the reactions of R^1MgBr with R^2HgBr or R^1HgBr with R^2MgBr [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 = C_6F_5, 2,3,4,5-C_6F_4H; 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 C_6F_5HgR occurred under the action of the Grignard reagent with the formation of C_6F_5MgX, which was not observed in the case of the above-mentioned arylmercury derivatives [1, 2].

Indeed, the interaction of C_6F_5HgEt with EtMgBr led to the formation of pentafluorophenylmagnesium bromide **6**,

Scheme 1.

$$\underset{\mathbf{1}}{C_6F_5HgCl} + EtMgBr \xrightarrow[22^{o}C,\ 3\ h]{Et_2O-THF} \underset{\mathbf{2a}}{C_6F_5HgEt} + \underset{\mathbf{3}}{(C_6F_5)_2Hg} + \underset{\mathbf{5}}{C_6F_5H} + \underset{\mathbf{4a}}{Et_2Hg}$$

$$\underset{\mathbf{1}}{C_6F_5HgCl} + PhMgBr \xrightarrow[22^{o}C,\ 5\ h]{Et_2O-THF} \underset{\mathbf{2b}}{C_6F_5HgPh} + \underset{\mathbf{3}}{(C_6F_5)_2Hg} + \underset{\mathbf{4b}}{PhHgCl}$$

Scheme 2.

$$\underset{\mathbf{2a},\ \mathbf{2b}}{C_6F_5HgR} + RMgBr \xrightarrow[22^{\circ}C,\ 3\ h]{Et_2O} \underset{\mathbf{6}}{C_6F_5MgBr} + \underset{\mathbf{7}}{(C_6F_5)_2Mg} + \underset{\mathbf{4a},\ \mathbf{4b}}{R_2Hg} \xrightarrow{H_2O} \mathbf{5} + \mathbf{4a},\ \mathbf{4b}$$

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

Scheme 3.

$$\underset{\mathbf{3}}{(C_6F_5)_2Hg} + RMgBr \xrightarrow[22^{\circ}C,\ 3\ h]{Et_2O} \underset{\mathbf{6}}{C_6F_5MgBr} + \underset{\mathbf{7}}{(C_6F_5)_2Mg} + \underset{\mathbf{2a},\ \mathbf{2b}}{C_6F_5HgR} + \underset{\mathbf{4a},\ \mathbf{4b}}{R_2Hg} \xrightarrow{H_2O} \mathbf{2} + \mathbf{5}$$

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

bis(pentafluorophenyl)magnesium **7**, and diethylmercury (Scheme 2). Similarly, the reaction of C_6F_5HgPh 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 C_6F_5HgPh, while the amount of C_6F_5HgEt remaining unchanged (^{19}F NMR). That fact evidenced significant effect of the substituent R in the starting C_6F_5HgR 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 Ar_FHgR from ArM (Ar_FM) and RHgX, the alternative approach based on the interaction of organomagnesium nucleophiles RMgBr with pentafluorophenylmercury derivatives gave a mixture of symmetrical and asymmetrical products C_6F_5HgR, $(C_6F_5)_2Hg$, and R_2Hg (R = Alk, Ar). The reaction involved perfluoromagnesium compounds formed via transmetalation of perfluoroarylmercury compounds with the Grignard reagents.

EXPERIMENTAL

$(C_6F_5)_2Hg$, C_6F_5HgPh [3], C_6F_5HgCl, and C_6F_5HgEt [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 C_6H_5F. 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 C_6F_5HgEt (0.09 mmol) and C_6F_5H (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 C_6F_5HgPh (0.16 mmol) and C_6F_5H (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 C_6F_5HgEt (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.

REFERENCES

1. Steinborn, D., Taube, R., Radeglia, R., and Hoebold, W., *J. Organomet. Chem.*, 1981, vol. 210, no. 2, p. 139. doi 10.1016/S0022-328X(00)82227-5
2. Kharasch, M.S., Marker, R., *J. Am. Chem. Soc.*, 1926, vol. 48, no. 12, p. 3130. doi 10.1021/ja01691a018
3. Chambers, R.D., Coates, G.E., Livingstone, J.G., and Musgrave, W.K.R., *J. Chem.* Soc., 1962, no. 11, p. 4367. doi 10.1039/JR9620004367
4. Burdon, J., Coe, P.L., Fulton, M., and Tatlow, J.C., *J. Chem.* Soc., 1964, no. 8, p. 2673. doi 10.1039/JR9640002673
5. Brooke, G.M., Chambers, R.D., Heyes, J., and Musgrave, W.K.R., *J. Chem.* Soc., 1964, no. 2, p. 729. doi 10.1039/JR9640000729
6. Bardin, V.V., *Magn. Res. Chem.*, 2018, vol. 56, no. 11, p. 1124. doi 10.1002/mrc.4755
7. Evans, D.F. and Khan, M.S., *J. Chem.* Soc., 1967A, no. 10, p. 1643. doi 10.1039/J19670001643
8. Pushkina, L.N., Stepanov, A.P., Zhukov, V.S., and Naumov, A.D., *Zh. Org. Khim.*, 1972, vol. 8, no. 3, p. 586.
9. Pushkina, L.N., Stepanov, A.P., Zhukov, V.S., and Naumov, A.D., *Org. Magn. Res.*, 1972, vol. 4, no. 5, p. 607. doi 10.1002/mrc.1270040503
10. Nöth, H. and Wrackmeyer, B., *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Berlin: Springer, 1978, p. 129.