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ORIGINAL PAPER

The preparation of pentafluorophenyldihaloboranes from pentafluorophenylmercurials C_6F_5HgR and BX_3: the dramatic dependence of the reaction direction on the ligand R

Vadim V. Bardin[1,2] · **Nicolay Yu. Adonin**[2,3]

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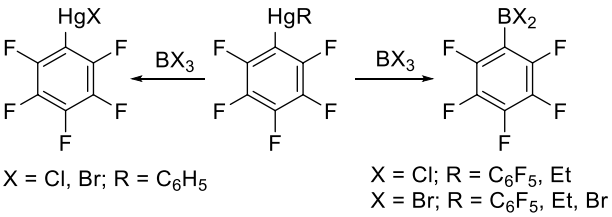
Abstract
In search of convenient preparations of $C_6F_5BX_2$ (X = Cl, Br), reactions of C_6F_5HgR (R = C_6F_5, C_6H_5, C_2H_5, Br and Cl) with BX_3 were studied. Under the action of BCl_3 the order of the C–Hg bond cleavage is $C_6F_5Hg–C_6H_5 > C_6F_5–HgC_2H_5 > C_6F_5–HgC_6F_5 >> C_6F_5–HgCl$. With more reactive BBr_3 the sequence is $C_6F_5Hg–C_6H_5 > C_6F_5–HgC_2H_5 \sim C_6F_5Hg–C_2H_5 > C_6F_5–HgC_6F_5 \geq C_6F_5–HgBr$. During the study we found the simple way to alkyldibromoboranes which is presented by the preparation of $C_2H_5BBr_2$ from C_2H_5HgBr and BBr_3. It is the second example of synthesis of alkylmercury derivative in an addition to the earlier reported formation of cyclopropylmercurials from di(cyclopropyl)mercury and BX_3.

Graphic abstract



Keywords Main group compounds · NMR spectroscopy · Transmetallation · Organometallic compounds

Introduction

Recently, we reported the successful *C*-alkylation of some phenols with olefins catalyzed with fluoro-containing phenyldifluoroboranes [1]. This demonstrates the perspectives of this class of organoboron compounds in Lewis acid-catalyzed processes. The obtained results prompted us to search the convenient preparations of polyfluorinated aryldichloroboranes and aryldibromoboranes, the stronger Lewis acids than their non-fluorinated analogues. Syntheses of the latter boranes are known for a long time, but majority of them cannot be applied for the preparation of polyfluorinated analogues because of the specific influence of many fluorine atoms in aromatic ring (see reviews [2, 3]). The first polyfluorinated arylboranes $C_6F_5BX_2$ (X = F, Cl, Br) and $(C_6F_5)_3B$ were synthesized in the sixties [4–7]. They remained the chemical exotic until the mid-eighties when outstanding properties of tris(pentafluorophenyl)borane as co-catalyst of the olefin polymerization was discovered. Now the number of publications about its applications in homogeneous catalysis of many processes exceeds two thousand.

Dedicated to Prof. Dr. Dr. H. C. H.-J. Frohn on the occasion of his 75th birthday.

✉ Vadim V. Bardin
bardin@nioch.nsc.ru

[1] N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, Acad. Lavrent'ev Ave., 9, 630090 Novosibirsk, Russia

[2] Novosibirsk State University, Pirogova Str., 2, 630090 Novosibirsk, Russia

[3] G. K. Boreskov Institute of Catalysis, SB RAS, Acad. Lavrent'ev Ave., 5, 630090 Novosibirsk, Russia

The catalytic properties of polyfluorinated aryldihaloboranes were not studied.

There are two practically available routes to Ar_FBX_2 (Ar_F is polyfluoroaryl moiety). The first is a reaction of C_6F_5HgAlk (Alk = CH_3, C_2H_5) with BCl_3 without solvent [6, 7] or with BBr_3 in CH_2Cl_2 [8]. The preparation of $C_6F_5BBr_2$ by long refluxing of C_6F_5HgBr and BBr_3 in toluene was claimed without description [9]. The second route is presented by the formation of $C_6F_5BCl_2$ from of $C_6F_5SnMe_3$ or $(C_6F_5)_2SnMe_2$ and boron trichloride (yields 96 and 74%, respectively) [4, 6], and $C_6F_5BBr_2$ from BBr_3 and $(C_6F_5)_2SnBu_2$ (yield 22%) [5]. The main disadvantage of the "tin" method is the difficult isolation aryldihaloboranes due to the close boiling points and the solubility of the reaction by-product, alkyltin halide. This is complicated by the high sensibility of both $C_6F_5BX_2$ and Alk_nSnX_{4-n} to moisture. The "mercury" method is devoid of these disadvantages. Mercurials XHgAlk are solid which are poorly soluble in non-polar organic solvents. They can be easily separated from the solutions of formed polyfluoroaryldihaloborane and reused in the synthesis of C_6F_5HgAlk without the environment pollution.

Being interested in pentafluorophenyldihaloboranes as perspective homogeneous catalysts, we studied reactions of easily available pentafluorophenylmercurials C_6F_5HgR (R = C_6F_5, C_6H_5, C_2H_5, Br, and Cl) with boron trichloride and boron tribromide to develop a convenient way to produce pentafluorophenyldichloroborane and pentafluorophenyldibromoborane in solution. To get an objective picture, these reactions were performed in weakly polar solvents (CH_2Cl_2, CH_2ClCH_2Cl) where arylmercurials (both substrates and products) are soluble. However, organomercury halides and mercury dihalides are low soluble in non-polar solvents, and at the end of reaction they can be removed from of the desired solution of aryldihaloboranes by dilution with hexane or benzene and the subsequent centrifugation.

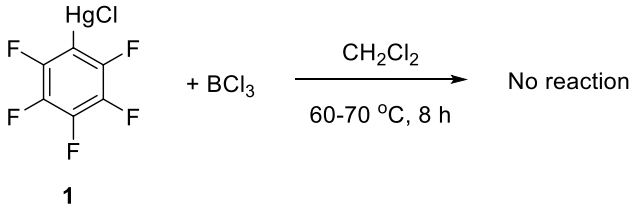
Results and discussion

Reactions with boron trichloride

Pentafluorophenylmercury chloride (**1**) does not react with BCl_3 being heated in sealed tube at 60–70 °C (Scheme 1). No reaction between bis(pentafluorophenyl)mercury (**2**) and BCl_3 in CH_2Cl_2 was observed at 22 °C over a period of 24 h. At higher temperature (60–70 °C) pentafluorophenyldichloroborane (**3**) and pentafluorophenylmercury chloride are formed (Scheme 2).

There are two possibilities of C–Hg bond cleavage for pentafluorophenyl(phenyl)mercury (**4**). Mixing **4** with excess BCl_3 in CH_2Cl_2 at 2–4 °C and subsequent warming the reaction mixture to room temperature showed unambiguously

Scheme 1



1

the formation of **1** and phenyldichloroborane. The same result was obtained at − 60 °C (Scheme 3).

The reaction of pentafluorophenyl(ethyl)mercury (**5**) with boron trichloride (twofold excess) in CH_2Cl_2 at − 60 °C for 6 h and subsequent warming to room temperature gives aryldichloroborane **3** and EtHgCl in quantitative yields. An addition of BCl_3 in CH_2Cl_2 to **5** at 2–4 °C and stirring at 22 °C also results in **3** and EtHgCl. Attempt to obtain bis(pentafluorophenyl)chloroborane (**6**) using excess of **5** (22 °C, 72 h) led to the incomplete conversion of C_6F_5HgEt to $C_6F_5BCl_2$ and $(C_6F_5)_2BCl$. The complete conversion of **5** to **6** was achieved after 1 week, although target compound was contaminated with the hydrolysis products such as C_6F_5H, $[(C_6F_5)_2B]_2O$, and $(C_6F_5)_2BOH$ (^{11}B, ^{19}F NMR) (Scheme 4).

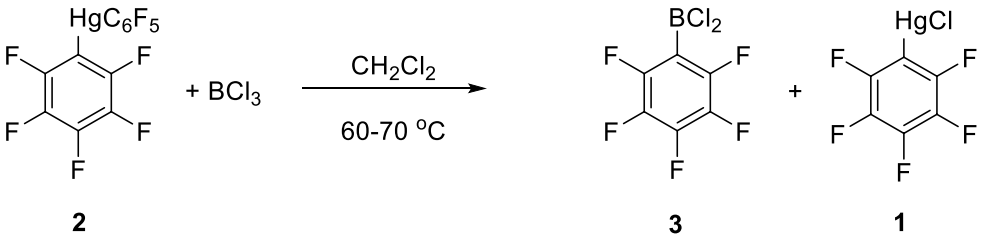
Reactions with boron tribromide

Pentafluorophenylmercury bromide (**7**) reacts with BBr_3 (1 equivalent) in DCE at 22 °C very slowly and after 24 h its conversion does not exceed 10–15%. Reflux of the reaction solution within 7 h leads to the precipitation of $HgBr_2$, but the complete conversion of **7**–**8** requires a longer period. The use of C_6F_5HgCl instead of C_6F_5HgBr and heating in sealed tube at the higher temperature results in a mixture of $C_6F_5BCl_nBr_{2-n}$ (n = 0–2) (^{11}B, ^{19}F NMR) that was confirmed by hydrolysis of these boranes to pentafluorophenylboronic acid (Scheme 5).

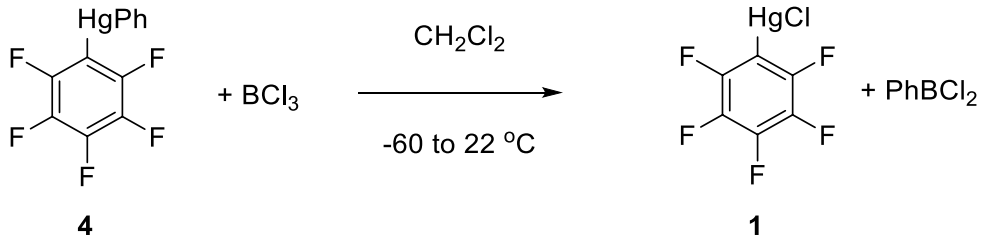
Taking into account the low reactivity of **7** towards BBr_3 the stepwise substitution of C_6F_5 groups in $(C_6F_5)_2Hg$ with bromine was expected. Actually, the treatment of **2** with BBr_3 leads to the slow disappearance of the substrate and formation of $C_6F_5BBr_2$ and C_6F_5HgBr. The complete conversion of **2** was achieved within 24 h. Using a more concentrated solution of **2** and excess of BBr_3 has a small effect. The desired borane **8** was obtained by heating of **2** with tribromoborane in DCE within 3 h (Scheme 6).

When $(C_6F_5)_2Hg$ is combined with one equivalent of BBr_3, the formation of bis(pentafluorophenyl)bromoborane (**9**) from intermediate **8** and **7** becomes possible. Unfortunately, this reaction proceeds slowly even at 120 °C in ampoule that points out the lower reactivity of $C_6F_5BBr_2$ with respect to reactivity of BBr_3 (Scheme 7).

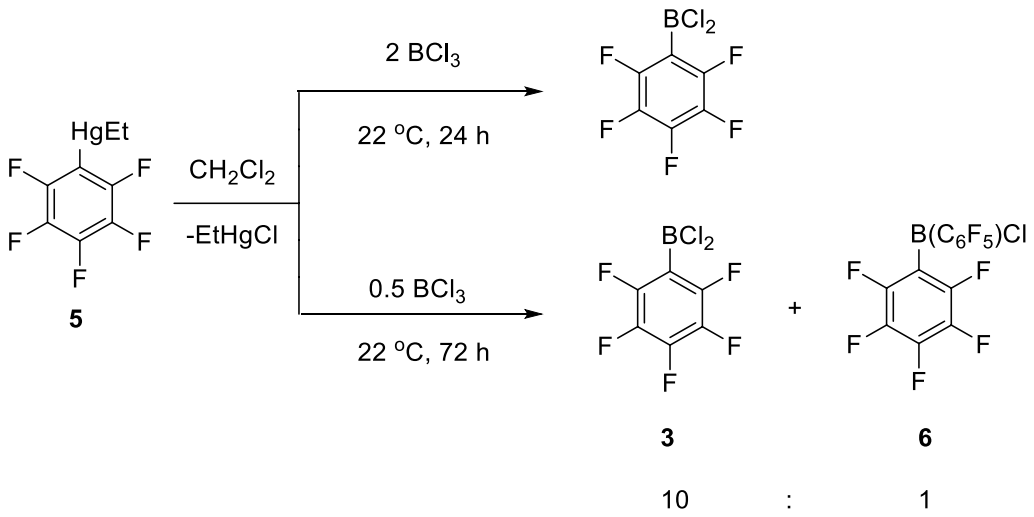
Scheme 2



Scheme 3



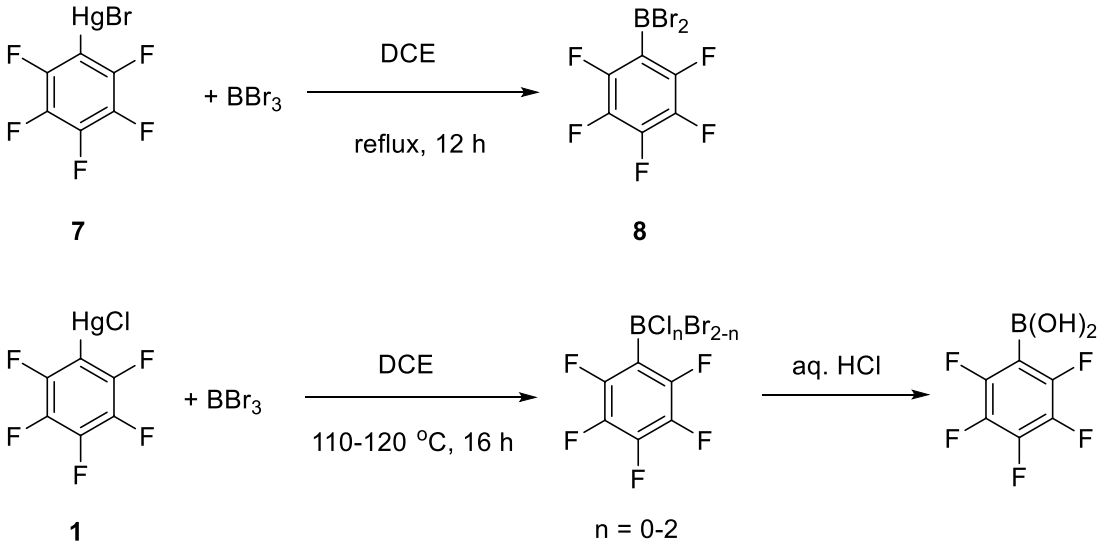
Scheme 4



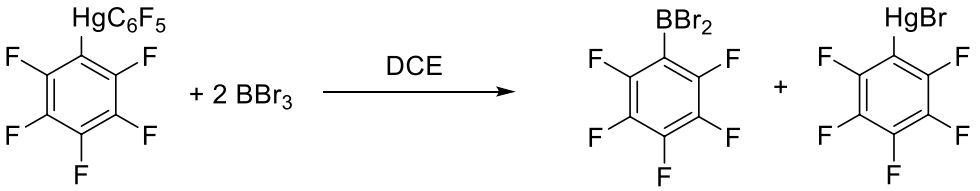
In contrast to **2**, reaction of arylmercurial **4** with BBr_3 proceeds quickly giving **7** and phenyldibromoborane (Scheme 8).

The result of interaction of pentafluorophenyl(ethyl) mercury with BBr_3 strongly depends on the reaction conditions. If $C_6F_5BCl_2$ can be obtained from **5** and neat BCl_3 at 22 °C [6, 7], the contact of neat BBr_3 with **5** at 22 °C caused vigorous reaction and formation of complex mixture. In addition, the fast and quantitative cleavage of Hg–Et bond and formation of **7** occurred when **5** was added to BBr_3 in toluene. Mixing of reagents in dichloromethane solution at 2–4 °C results in precipitate and colorless mother liquor that contained **8**, **7**, $EtBBr_2$, and residual BBr_3, but no further reaction was observed for the next 72 h at 22 °C (^{11}B, ^{19}F NMR). Reverse the order of mixing, an addition of BBr_3 to **5**, reduces the amount of **7**, but not significantly. The closely related result was obtained when BBr_3 was added to **5** at − 55 °C. Desired product **8** was prepared by addition of **5** to BBr_3 (1:1) in CH_2Cl_2 at − 55 °C, e.g. by reproduction of reported procedure [8] (Scheme 9).

Scheme 5

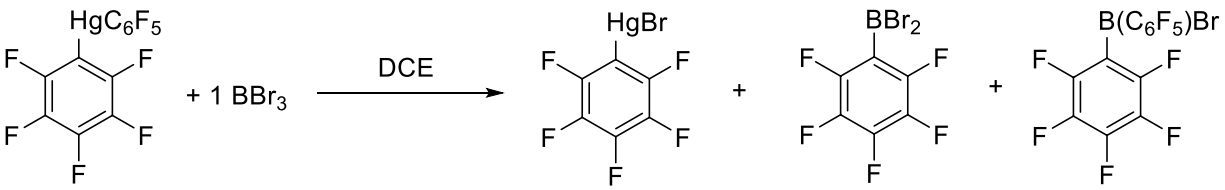


Scheme 6



22 °C, 24 h:	1	:	1
85 °C, 3 h:	1	:	0

Scheme 7

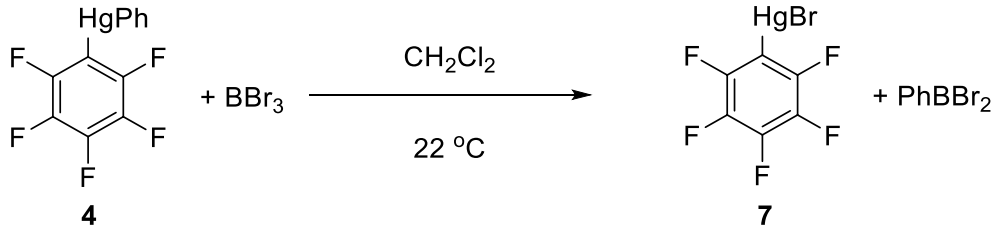


80 °C, 9 h:	9	:	6	:	1
120 °C, 17 h:	0.7	:	0.5	:	1

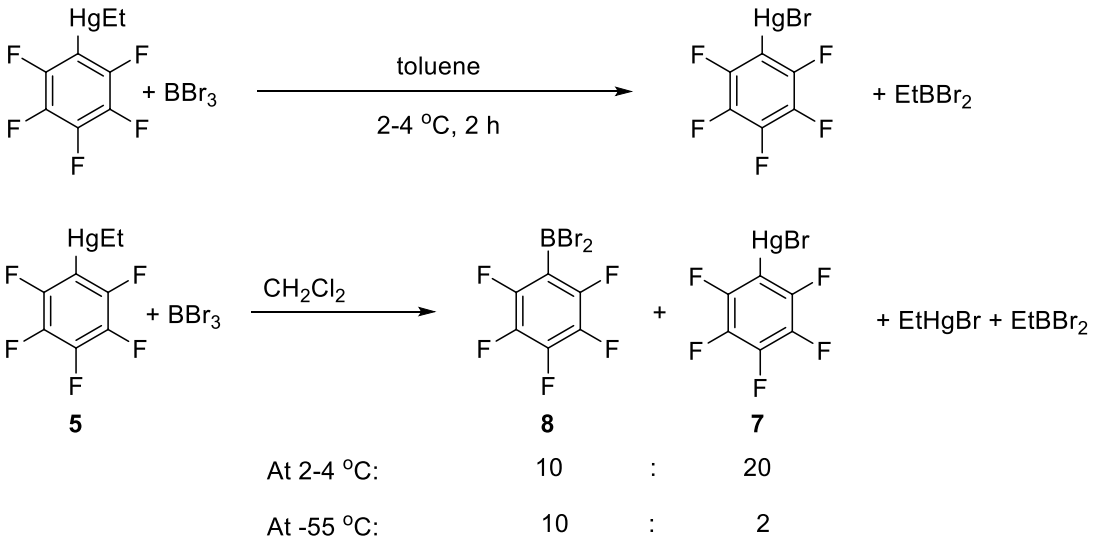
The obtained picture reveals the significant difference of reactivity of C_6F_5HgR from that for the non-fluorinated analogues towards trihaloboranes. This is well-illustrated by comparison of our results (Schemes 1 and 2) and the reported reaction conditions for the related phenylmercury derivatives [10, 11] (Scheme 10). It is clear that the removal of aryl groups from the mercury surround occurs under milder conditions than the removal of the corresponding polyfluoroaryl groups.

Based on our results shown above we could do some considerations about the reaction pathways. Likely, the driving force of reaction is the affinity of mercury to halide anion that increases in the order: F < Cl < Br < I, and this coincides with the relative reactivity of trihaloboranes: $BCl_3 < BBr_3$. It seems that the C–Hg bond cleavage is the

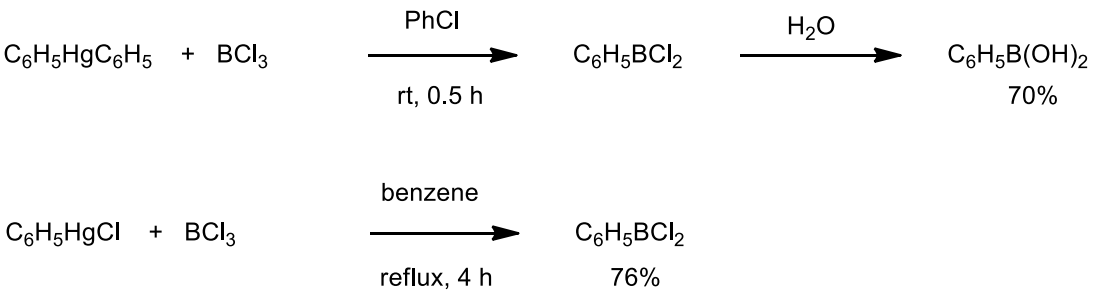
Scheme 8



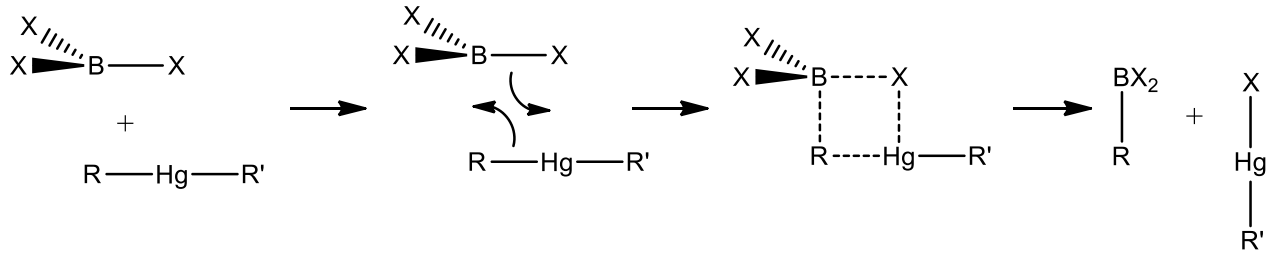
Scheme 9



Scheme 10



Scheme 11



Scheme 12

result of concerted reaction with BX_3 with the coordination of halide atom X to mercury. There are two possible modes of such cleavage in the case of asymmetric diorganylmercury, RHgR'. It is logical to assume that the preferred site for coordinating the electron-deficient boron atom is a more electron-rich carbon atom (Scheme 11).

In the reactions with BCl_3 the carbon-mercury bonds cleave selectively in the order: $C_6F_5Hg–C_6H_5 > C_6F_5–HgC_2H_5 > C_6F_5–HgC_6F_5$. In the case of BBr_3 bond Hg–C_6H_5 cleaves faster than bond Hg–C_6F_5, but the interaction of $C_6F_5HgC_2H_5$ with tribromoborane proceeds on both channels (Scheme 9). For example, the carbon atom of CH_2 moiety is the more kinetically attractive reaction center than carbon C-1 of the pentafluorophenyl group (at least, at room temperature). Evidently, this is consistent with the lower reactivity of C_6F_5HgBr (Scheme 5) compared with that of C_2H_5HgBr which reacts with BBr_3 at room temperature (Scheme 12).

We tried to find other examples of the preparation of alkylboranes from alkylmercurials AlkHgR′ (R′ = halogen or any organyl group) and BX_3. To our surprise, there is only one communication that describes syntheses of cyclopropylboranes $C_3H_5BX_2$ by unfreezing bis(cyclopropyl)mercury and Me_2BCl, BCl_3 or BF_3 from − 196 °C [12]. Thus, the above preparation of $EtBBr_2$ is the second example of such process.

Finally, two publications on acidolysis of R_2Hg (R = CH_2=CH, C_6H_5, C_nH_{2n+1}) by anhydrous HCl, HBr, or H_2SO_4 in DMSO-dioxane should be mentioned. Based on the kinetic measurements, Dessy et al. [13, 14] outlined the following sequences of the reactivity: R = CH_2=CH > C_6H_5 >> C_2H_5 and HBr > HCl. They also suggested that reactions proceed via the concerted mechanism rather than simple attack by H^+. In the other words, scheme of acidolysis with Brønsted acids, HCl and HBr, has the close similarity with assumed route of the C–Hg bond cleavage with Lewis acids, BX_3 (Scheme 11).

Conclusion

1. $C_6F_5HgC_2H_5$ is the most convenient arylmercurial reagent among the tested ones for the preparation of $C_6F_5BCl_2$. Its reaction with BBr_3 in CH_2Cl_2 at low temperature can be also employed for the synthesis of $C_6F_5BBr_2$, but the desired product can be contaminated with C_6F_5HgBr.
2. Preferential route to $C_6F_5BBr_2$ is heating C_6F_5HgBr with BBr_3 (excess) in an appropriate solvent. Another arylmercurials **1**, **2**, **4**, and **5** are not convenient substrates.
3. Reaction of all tested C_6F_5HgR with BX_3 (X = Cl, Br) is not suitable for the preparation of $(C_6F_5)_2BX$ due to the low reactivity of C_6F_5HgX towards $C_6F_5BX_2$.
4. The observed alkyl-mercury bond cleavage in C_6F_5HgEt and EtHgBr by BBr_3, together with early communication [12], proves the possibility of preparation of alkyldibromoborane from alkylmercurials.

Experimental

The NMR spectra were recorded on a Bruker Avance 300 (^{1}H at 300.13 MHz and ^{19}F at 282.40 MHz) and Avance 600 (^{11}B at 192.60 MHz and ^{199}Hg at 107.51 MHz) spectrometers. The chemical shifts are referenced to TMS (^{1}H), 15% BF_3 OEt_2 (v/v) in $CDCl_3$ (^{11}B), CCl_3F (^{19}F, with C_6F_6 as secondary reference (− 162.9 ppm)), and $(CH_3)_2Hg$ (neat) (^{199}Hg), respectively.

Ether and THF were distilled over sodium and stored over it. Dichloromethane and 1,2-dichloroethane (DCE) were distilled over P_2O_5 and stored over zeolites. Organomercurials C_6F_5HgCl (**1**), C_6F_5HgBr (**7**), C_6F_5HgEt (**5**) [15], $(C_6F_5)_2Hg$ (**2**) [16] were prepared as described. C_6F_5HgPh (**4**) [16] and C_6H_5HgBr [17, 18] were prepared on the modified procedures. BCl_3 and BBr_3 were used as supplied. Quantitative analysis of reaction mixtures was performed by the ^{19}F NMR spectroscopy with quantitative internal reference C_6H_5F. The known aryl(halo)boranes **3**, **6**, **8**, **9** [3], $C_2H_5BBr_2$, $C_6H_5BCl_2$, and $C_6H_5BBr_2$ [19] were identified on the ^{11}B and ^{19}F NMR spectra.

Phenylmercury bromide Mercury dibromide (27.1 g, 10 mmol) was suspended in 100 cm^3 ether and a solution of C_6H_5MgBr [from 12.0 g C_6H_5Br (76 mmol) and 1.88 g Mg (77 mmol)] in 50 cm^3 ether was added gradually to keep gentle boiling. White suspension was refluxed for 4 h, cooled and colorless ethereal phase was decanted. Residue was washed with hot diluted HCl, with water, with 30 cm^3 ethanol and with 30 cm^3 ether. Then white powder was dried on air and at 100–105 °C (oil bath) to yield C_6H_5HgBr (24 g). ^{1}H NMR (acetone-d_6): $\delta = 7.33$ [d, $^3J(H^2, H^3) = 6.8$ Hz, 2H, $H^{2,6}$], 7.17 [t, $^3J(H^4, H^{3,5}) = 7.1$ Hz, 1H, H^4], 7.10 (m, 2H, $H^{3,5}$) ppm; ^{199}Hg{H} NMR (acetone-d_6): $\delta = -1305$ ppm.

Pentafluorophenyl(phenyl)mercury (4) Phenylmercury bromide (2.89 g, 8 mmol) was suspended in 10 cm^3 THF and a solution of C_6F_5MgBr [from 2.53 g C_6F_5Br (10 mmol) and 0.343 g Mg (14 mmol)] in 27 cm^3 ether was added gradually. White suspension was refluxed for 3 h, cooled and treated with water. Organic phase was decanted and aqueous one was extracted with ether. Combined extract was washed with brine acidified with HCl, and dried with $MgSO_4$. Solvent was evaporated to yield brownish powder. Crystallization from CCl_4 gave needles (2.4 g). ^{1}H NMR (acetone-d_6): $\delta = 7.34$ (d, $^3J(H^2, H^3) = 6.8$ Hz, 2H, $H^{2,6}$), 7.20 (dd, 2H, $H^{3,5}$), 7.05 [t, $^3J(H^4, H^{3,5}) = 7.4$ Hz, 1H, H^4] ppm; ^{19}F NMR (acetone-d_6): $\delta = -118.0$ [md, $^3J(F^{2,6}, Hg) = 358$ Hz, 2F, $F^{2,6}$], -155.0 [t, $^3J(F^4, F^{3,5}) = 19.3$ Hz, 1F, F^4], -160.6 [md, $^4J(F^{3,5}, Hg) = 64$ Hz, 2F, $F^{3,5}$] ppm; ^{199}Hg{H} NMR (acetone-d_6): $\delta = -884$ [tt, $^3J(Hg, F^{2,6}) = 360$ Hz, $^4J(Hg, F^{3,5}) = 64$ Hz] ppm.

Attempted reaction of C_6F_5HgCl with BCl_3 in CH_2Cl_2 Solution of 516 mg C_6F_5HgCl (1.28 mmol) and BCl_3 (1.9 mmol) in 5.5 cm^3 CH_2Cl_2 was kept into sealed tube at 60–80 °C (bath) for 8 h. No reaction occurred (^{19}F NMR).

Reaction of $(C_6F_5)_2Hg$ with BCl_3 Solution of 290 mg $(C_6F_5)_2Hg$ (**2**, 0.54 mmol) and BCl_3 (0.95 mmol) in 7 cm^3 CH_2Cl_2 was kept at 22 °C for 24 h, but no reaction occurred (^{19}F NMR). It was heated into sealed tube at 60–70 °C (bath) for 12 h. The solution contained C_6F_5HgCl (**1**), $C_6F_5BCl_2$ (**3**) (1:1), and residual BCl_3 (^{11}B, ^{19}F NMR).

Reactions of C_6F_5HgPh with BCl_3 Cold (2–4 °C) 0.95 M solution of BCl_3 in CH_2Cl_2 (2.0 cm^3, 1.9 mmol) was added into cold (2–4 °C) (bath) stirred solution of 372 mg C_6F_5HgPh (**4**, 0.83 mmol) in 5 cm^3 CH_2Cl_2. After 24 h at 22 °C, solution contained C_6F_5HgCl (**1**, 0.81 mmol), $C_6H_5BCl_2$, and BCl_3 (^{11}B, ^{19}F NMR).

Cold (− 60 °C) 0.95 M BCl_3 in CH_2Cl_2 (1.0 cm^3, 0.95 mmol) was added into cold (− 60 °C) (bath) stirred solution of 506 mg C_6F_5HgPh (**4**, 0.50 mmol) in 3 cm^3 CH_2Cl_2 and kept at − (60–55) °C for 5 h. Then the reaction mixture was thawed to room temperature overnight. It contained C_6F_5HgCl (**1**, 0.46 mmol), $C_6H_5BCl_2$, and BCl_3 (^{11}B, ^{19}F NMR).

Reactions of C_6F_5HgEt with BCl_3 Solution of 405 mg C_6F_5HgEt (**5**, 1.0 mmol) in 1 cm^3 CH_2Cl_2 was added into cold (− 60 °C) (bath) stirred 2.1 cm^3 0.95 M solution of BCl_3 in CH_2Cl_2 (2.0 mmol) diluted with 2 cm^3 CH_2Cl_2. After 1 h, white suspension was formed. It was stirred at − (45–55) °C for 6 h, and allowed to warm to 22 °C overnight. The mother liquor over precipitate contained $C_6F_5BCl_2$ (**3**, 0.80 mmol) (^{19}F NMR) and EtHgCl (0.38 mmol) (^{1}H NMR). After dilution with 6 cm^3 hexane, precipitated EtHgCl was separated by centrifugation.

Solution 0.95 M BCl_3 in CH_2Cl_2 (1.2 cm^3, 1.11 mmol) was added into cold (2–4 °C) (bath) stirred solution of 243 mg C_6F_5HgEt (**5**, 0.61 mmol) in 7 cm^3 CH_2Cl_2. The colorless solution was stirred at 22 °C for 24 h. It contained $C_6F_5BCl_2$ (**3**, 0.59 mmol) and EtHgCl (^{1}H, ^{19}F NMR). The latter was precipitated by cooling to − (40–50) °C and subsequent decantation of the mother liquor under an atmosphere of dry argon.

Solution 0.95 M BCl_3 in CH_2Cl_2 (1.6 cm^3, 1.5 mmol) was added into cold (− 60 °C) (bath) stirred solution of 1.18 g C_6F_5HgEt (**5**, 2.97 mmol) in 7 cm^3 CH_2Cl_2. The reaction mixture was stirred at − (60–55) °C for 6 h, and allowed to warm to 22 °C overnight. The mother liquor contained C_6F_5HgEt (**5**), $C_6F_5BCl_2$ (**3**), and $(C_6F_5)_2BCl$ (**6**) (2:10:1). After 72 h it contained $C_6F_5BCl_2$, $(C_6F_5)_2BCl$, $[(C_6F_5)_2B]_2O$, and C_6F_5H (10:6:6:6). After 1 week, $(C_6F_5)_2BCl$, $[(C_6F_5)_2B]_2O$, $(C_6F_5)_2BOH$, and C_6F_5H were formed in ratio 2:3:1:3 (^{19}F NMR).

$[(C_6F_5)_2B]_2O$ ^{19}F NMR (CD_2Cl_2): $\delta = -132.3$ (m, $8F^{2,6}$), -146.2 [tt, $^3J(F^4, F^{3,5}) = 20.1$ Hz, $^4J(F^4, F^{2,6}) = 5.3$ Hz, $4F^4$], -161.2 (m, $8F^{3,5}$) ppm (lit. [20]: $\delta = -132.12$, -145.99, -161.14 ppm); ^{11}B NMR (CD_2Cl_2): $\delta = 38.6$ ppm.

$(C_6F_5)_2BOH$ ^{19}F NMR (CD_2Cl_2): $\delta = -132.9$ (m, $4F^{2,6}$), -148.7 [t, $^3J(F^4, F^{3,5}) = 18.6$ Hz, $2F^4$], -161.2 (m, $4F^{3,5}$) ppm (lit. [20]: $\delta = -132.78$, -148.28, -160.70 ppm); ^{11}B NMR (CD_2Cl_2): $\delta = 40.5$ ppm (lit. [21]: $\delta = 40.2$ ppm).

Reaction of C_6F_5HgBr with BBr_3 Solution of 695 mg C_6F_5HgBr **7** (1.55 mmol) and 409 mg BBr_3 (1.63 mmol) in 5 cm^3 DCE was refluxed 7 h to form suspension. The mother liquor showed signals of $C_6F_5BBr_2$ (**8**, 1.22 mmol) and C_6F_5HgBr (**7**, 0.13 mmol, 90% conversion). After an additional reflux for 5 h, the mother liquor was decanted. The ^{19}F NMR spectrum showed signals of $C_6F_5BBr_2$ (1.47 mmol, 95% yield).

Reaction of C_6F_5HgCl with BBr_3 C_6F_5HgCl (**1**, 197 mg, 0.48 mmol) and 120 mg BBr_3 (0.48 mmol) in 3 cm^3 DCE were heated in a sealed tube at 110–120 °C (bath) for 16 h. A probe of the mother liquor over precipitate showed signals at − (128.5–129.8) (four multiplets), − (145.0–146.4) (four triplets), and − 161 ppm (overlapped multiplets) in 2:1:2 ratio, which were attributed to $C_6F_5BCl_nBr_{2-n}$ ($n = 0$–2) (0.42 mmol) (^{19}F NMR). In the ^{11}B NMR spectrum signals of $C_6F_5BBr_2$ (**8**) at 53.5 ppm and $C_6F_5BCl_2$ (**3**) at 52.7 ppm were identified. In addition, traces of C_6F_5HgBr, C_6F_5H, BCl_3, BCl_2Br, and $BClBr_2$ were found (^{11}B, ^{19}F NMR). Additional evidence of arylboranes formation was the production of $C_6F_5B(OH)_2$ (0.38 mmol) by hydrolysis of this solution.

Reactions of $(C_6F_5)_2Hg$ with BBr_3 Solution of 137 mg $(C_6F_5)_2Hg$ (**2**, 0.25 mmol) and 125 mg BBr_3 (0.50 mmol) in 3 cm^3 DCE was kept at 22 °C for 4 h. The colorless solution showed signals of $(C_6F_5)_2Hg$ (0.05 mmol), C_6F_5HgBr (**7**, 0.19 mmol) and $C_6F_5BBr_2$ (**8**, 0.13 mmol). After 24 h, the solution contained C_6F_5HgBr (0.22 mmol) and $C_6F_5BBr_2$ (0.16 mmol) (^{19}F NMR).

Solution of 282 mg $(C_6F_5)_2Hg$ (**2**, 0.52 mmol) and 403 mg BBr_3 (1.61 mmol) in 1.6 cm^3 DCE was kept at 22 °C for 18 h. The colorless solution showed signals of C_6F_5HgBr (**7**, 0.37 mmol) and $C_6F_5BBr_2$ (**8**, 0.68 mmol). After 42 h, the solution contained C_6F_5HgBr (0.20 mmol) and $C_6F_5BBr_2$ (0.74 mmol) (^{19}F NMR). Arylmercurial **7** was removed by dilution with 5 cm^3 benzene and subsequent centrifugation.

Solution of 282 mg $(C_6F_5)_2Hg$ (**2**, 0.52 mmol) and 403 mg BBr_3 (1.61 mmol) in 1.6 cm^3 DCE was kept at 80–85 °C for 3 h and left at 22 °C overnight. The mother liquor was decanted, diluted with 10 cm^3 DCE, and 8 cm^3 of a mixture of DCE (b.p.: 84 °C) and BBr_3 (b.p.: 89 °C) was distilled off under reduced pressure to give a solution of $C_6F_5BBr_2$ (**8**, 1.00 mmol) free of BBr_3 (^{11}B, ^{19}F NMR).

Solution 0.25 M BBr_3 in DCE (3 cm^3, 0.75 mmol) was added into the solution of 400 mg $(C_6F_5)_2Hg$ (**2**, 0.75 mmol) in 2 cm^3 DCE and stirred at 75–80 °C for 9 h. A probe showed signals of C_6F_5HgBr (**7**, 0.70 mmol), $C_6F_5BBr_2$ (**8**, 0.47 mmol), and $(C_6F_5)_2BBr$ (**9**, 0.08 mmol). Heating at 120 °C in a sealed tube for 17 h gave C_6F_5HgBr (0.22 mmol), $C_6F_5BBr_2$ (0.14 mmol), and $(C_6F_5)_2BBr$ (0.31 mmol) (^{11}B, ^{19}F NMR).

Reaction of C_6F_5HgPh with BBr_3 Solution 0.65 M BBr_3 in CH_2Cl_2 (1 cm^3, 0.65 mmol) was added into cold (1–4 °C) (bath) solution of 240 mg C_6F_5HgPh (**4**, 0.54 mmol) in 2 cm^3 CH_2Cl_2. The resulted solution was stirred in ice bath for 0.5 h, then at 22 °C for 3 h. The ^{11}B and ^{19}F NMR spectra showed signals of C_6F_5HgBr (**7**, 0.49 mmol) and $PhBBr_2$.

Reactions of C_6F_5HgEt with BBr_3 BBr_3 (1.52 g, 6.1 mmol) was added dropwise to 1.00 g neat C_6F_5HgEt (**5**, 2.5 mmol). Vigorous reaction occurred. The products were dissolved in 4 cm^3 CH_2Cl_2. According to the ^{19}F NMR spectrum, solution contained several pentafluorophenylboranes.

Solution of 757 mg C_6F_5HgEt (**5**, 1.9 mmol) in 3 cm^3 toluene was added into cold (1–4 °C) (bath) solution of 733 mg BBr_3 (2.9 mmol) in 13 cm^3 toluene. The solution was stirred in ice bath for 2 h. The ^{19}F NMR spectrum showed signals of C_6F_5HgBr (**7**) while $C_6F_5BBr_2$ was not detected.

Solution of 1.36 g C_6F_5HgEt (**5**, 3.43 mmol) in 3 cm^3 CH_2Cl_2 was added into cold (2–4 °C) (bath) solution of 1.22 g BBr_3 (4.84 mmol) in 13 cm^3 CH_2Cl_2. Immediately white suspension was formed. It was stirred in ice bath for 2 h. Probe of the mother liquor contained C_6F_5HgBr, $C_6F_5BBr_2$ (2:1), $EtBBr_2$, and BBr_3 (^{11}B, ^{19}F NMR). No changes proceeded for the next 72 h.

Cold (2–4 °C) 0.65 M BBr_3 in CH_2Cl_2 (1 cm^3, 0.65 mmol) was added into cold (2–4 °C) (bath) solution of 514 mg C_6F_5HgEt (**5**, 0.52 mmol) in 2 cm^3 CH_2Cl_2. The formed white suspension was stirred in ice bath for 2 h and left overnight. The mother liquor contained C_6F_5HgBr (**7**) and $C_6F_5BBr_2$ (**8**) (1:1), a few $(C_6F_5)_2BBr$ (**9**), $EtBBr_2$, and BBr_3. Exposition on wet air for 2 h led to partial hydrolysis and formation of $C_6F_5B(OH)_2$ and $EtB(OH)_2$ (^{11}B, ^{19}F NMR).

Solution 0.65 M BBr_3 in CH_2Cl_2 (1 cm^3, 0.65 mmol) was added into cold (− 55 °C) (bath) solution of 199 mg C_6F_5HgEt (**5**, 0.50 mmol) in 2.5 cm^3 CH_2Cl_2. The formed white suspension was allowed to warm to 22 °C within 3 h. The mother liquor contained C_6F_5HgBr and $C_6F_5BBr_2$ (1:1), $EtBBr_2$, and BBr_3 (^{11}B, ^{19}F NMR).

Solution of 1.14 g C_6F_5HgEt (**5**, 2.87 mmol) in 1 cm^3 CH_2Cl_2 was added slowly into cold (− 55 °C) (bath) solution of 756 mg BBr_3 (3.0 mmol) in 4 cm^3 CH_2Cl_2. Immediately white suspension was formed. It was stirred at − 55 °C for 10 min, and allowed to warm to 22 °C within 2 h. The ^{19}F NMR spectrum of the mother liquor showed signals of $C_6F_5BBr_2$ and an admixture of C_6F_5HgBr and $(C_6F_5)_2BBr$.

Reaction of C_2H_5HgBr with BBr_3 Suspension of 304 mg C_2H_5HgBr (1.0 mmol) and 268 mg BBr_3 (1.0 mmol) in 2 cm^3 DCE was stirred at 22 °C for 3 h. The solution of the formed $C_2H_5BBr_2$ (0.8 mmol) was decanted under an argon atmosphere (^1H, ^{11}B, and ^{19}F NMR).

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