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Synthesis and characterization of aryl(trifluoromethyl)bismuth compounds $(R-C_6H_4)_{3-n}Bi(CF_3)_n$ [R = H, 4-CH_3, 4-CF_3, 3-F, 4-F; $n = 1$ and 2] and the reactions of $(C_6H_5)_{3-n}Bi(CF_3)_n$ [$n = 0-3$] with benzoylpyridinium chloride★

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Abstract

The partly new derivatives $(R-C_6H_4)BiBr_2$ and $(R-C_6H_4)_2BiCl$ (R = 4-CH_3, 4-CF_3, 3-F, 4-F) have been prepared from the redistribution reactions of the corresponding triarylbismuth compounds with $BiBr_3$ and $BiCl_3$, respectively. Metathesis reactions of these substrates with $Cd(CF_3)_2$ complexes yielded the new aryl(trifluoromethyl)bismuth compounds $(R-C_6H_4)_{3-n}Bi(CF_3)_n$ ($n = 1$ and 2). The mono(trifluoromethyl) derivatives are quite stable towards dismutations, whereas the bis(trifluoromethyl) compounds rapidly redistribute to give $(R-C_6H_4)_2Bi(CF_3)$ and $Bi(CF_3)_3$. Comparative reactions of $(C_6H_5)_{3-n}Bi(CF_3)_n$ with benzoylpyridinium chloride showed that the mixed derivatives preferentially transfer the phenyl group to yield benzophenone. Reactions of R_3Bi with benzoylpyridinium chloride selectively give the corresponding phenone in good yield.

Keywords: Synthesis; Aryl(trifluoromethyl)bismuth compounds; Benzoylpyridinium chloride; NMR spectroscopy; Inductive parameters; Resonance parameters; Metathesis reactions

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1. Introduction

Although triorganobismuth compounds [1] and tris(perfluoro-organo)bismuth derivatives [2] are well known, less has been published about mixed organo-perfluoro-organo derivatives of this element.

In 1963 Bell et al. described a series of mixed methyl(perfluoroalkyl)bismuth derivatives as products of the reactions of $(CH_3)_3Bi$ with perfluoro-iodoalkanes [3]. These compounds were found to be very sensitive to oxygen and to begin to decompose below their boiling points. In a preliminary communication we described the successful synthesis of $(C_6H_5)_{3-n}Bi(CF_3)_n$ ($n = 1$ and 2) [4].

Reactions of triarylbismuth with inorganic and organic substrates have been the subject of many investigations [5]. It was found that these compounds can be regarded as powerful arylating reagents in the presence as well as in the absence of catalysts.

The oxidation of tris(perfluoro-organo)bismuth derivatives has been studied for $Bi(CF_3)_3$ and $Bi(C_6F_5)_3$ in reactions with elemental halogens, interhalogen compounds and xenon(II) derivatives [6]. During these investigations the perfluoro-organo derivatives turned out to react as polar perfluoro-organo group-transfer reagents; only reactions of $Bi(C_6F_5)_3$ with XeF_2 or fluoroxenon hexafluorometallates yielded the oxidation product $Bi(C_6F_5)_3F_2$.

In an extension of our previous work on the reaction behaviour of bismuth derivatives containing perfluoro-organo groups, we herein report the synthesis of a series of new mixed aryl(trifluoromethyl)bismuth derivatives. Transfer reactions in the benzoyl chloride/pyridine system have been studied for $(C_6H_5)_{3-n}Bi(CF_3)_n$ ($n = 0$–3).

★Dedicated to Professor L.M. Yagupolskii on the occasion of his 70th birthday.

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2. Results and discussion

2.1. *Synthesis of* $(R-C_6H_4)_{3-n}Bi(CF_3)_n$ *(n = 1 and 2; R = 4-CH₃, 4-CF₃, 3-F, 4-F)*

Arylbismuth halides can easily be prepared from redistribution reactions of the corresponding triaryl derivative and the bismuth trihalide in diethyl ether solution [7]. By analogy to previous reactions, new derivatives containing a partly fluorinated phenyl group could be prepared.

$$(R-C_6H_4)_3Bi + 2BiBr_3 \longrightarrow 3(R-C_6H_4)BiBr_2 \quad (1)$$

$$2(R-C_6H_4)_3Bi + BiCl_3 \longrightarrow 3(R-C_6H_4)_2BiCl \quad (2)$$

$$(R = 4\text{-}CF_3,\ 3\text{-}F,\ 4\text{-}F)$$

In a similar manner as observed for arylbismuth carboxylates [8], the diaryl derivatives in acetonitrile solution are quite stable towards redistribution reactions forming $(R-C_6H_4)_3Bi$ and $(R-C_6H_4)BiBr_2$, whereas the monoaryl compounds rapidly dismutate to give the diaryl derivative and the bismuth trihalide.

$$2(R-C_6H_4)BiX_2 \rightleftharpoons (R-C_6H_4)_2BiX + BiX_3 \quad (3)$$

$$2(R-C_6H_4)_2BiX \rightleftharpoons (R-C_6H_4)_3Bi + (R-C_6H_4)BiX_2 \quad (4)$$

$$(X = Cl,\ Br)$$

As a result of these equilibria, the metathesis reactions of the halides with $Cd(CF_3)_2$ complexes do not proceed very selectively (complexing CH_3CN is omitted in Eqs. (5) and (6)).

$$2(R-C_6H_4)_2BiCl + Cd(CF_3)_2 \longrightarrow 2(R-C_6H_4)_2Bi(CF_3) + CdCl_2 \quad (5)$$

$$(R-C_6H_4)BiBr_2 + Cd(CF_3)_2 \longrightarrow (R-C_6H_4)Bi(CF_3)_2 + CdBr_2 \quad (6)$$

In all cases product mixtures were obtained containing $(R-C_6H_4)_{3-n}Bi(CF_3)_n$ (n = 1–3). The compositions of the product mixtures are summarized in Table 1.

The formation of these mixtures can be explained by the redistribution equilibria of the halides as well as of the trifluoromethyl derivatives. Therefore, redistribution equilibria formulated for the carboxylates [8], the non-fluorinated analogues [9] and the halides, as mentioned above, can be applied.

From the reaction mixtures, the products could be isolated by fractional distillation in high vacuum. With the exception of $(4\text{-}CH_3C_6H_4)Bi(CF_3)_2$, all compounds could be obtained as pure, extremely air-sensitive, colourless oils.

The compounds $(R-C_6H_4)_2Bi(CF_3)$ may be stored as the pure product or in acetonitrile solution for several days without any ^{19}F NMR spectroscopical hints for redistribution equilibria. The derivatives $(R-C_6H_4)Bi(CF_3)_2$ can also be isolated by distillation in vacuo, but redistribution reactions occur more rapidly. In all cases, the rate of redistribution of the isolated $(R-C_6H_4)Bi(CF_3)_2$ compounds depends on the substituent at the phenyl group; qualitatively, the redistribution rate increases in the series $4\text{-}CF_3C_6H_4 < 4\text{-}FC_6H_4 \approx 3\text{-}FC_6H_4 < C_6H_5 < 4\text{-}CH_3C_6H_4$.

Table 1
Reaction times, yields and compositions of the product mixtures of the reactions of $(R-C_6H_4)_{3-n}BiX_n$ (n = 1 and 2) with $Cd(CF_3)_2 \cdot 2CH_3CN$

Substrate	Time (d)	Total yield (%)	Composition of product mixture (as determined from ^{19}F NMR spectra) (%)	
$(4\text{-}CH_3C_6H_4)BiBr_2$	2	78	$(4\text{-}CH_3C_6H_4)_2Bi(CF_3)$	33
			$(4\text{-}CH_3C_6H_4)Bi(CF_3)_2$	42
			$Bi(CF_3)_3$	25
$(3\text{-}FC_6H_4)BiBr_2$	3	87	$(3\text{-}FC_6H_4)_2Bi(CF_3)$	21
			$(3\text{-}FC_6H_4)Bi(CF_3)_2$	66
			$Bi(CF_3)_3$	13
$(4\text{-}FC_6H_4)BiBr_2$	3	85	$(4\text{-}FC_6H_4)_2Bi(CF_3)$	29
			$(4\text{-}FC_6H_4)Bi(CF_3)_2$	68
			$Bi(CF_3)_3$	3
$(4\text{-}CF_3C_6H_4)BiBr_2$	5	92	$(4\text{-}CF_3C_6H_4)_2Bi(CF_3)$	8
			$(4\text{-}CF_3C_6H_4)Bi(CF_3)_2$	90
			$Bi(CF_3)_3$	2
$(4\text{-}CH_3C_6H_4)_2BiCl$	5	90	$(4\text{-}CH_3C_6H_4)_2Bi(CF_3)$	98
			$(4\text{-}CH_3C_6H_4)Bi(CF_3)_2$	2
			$Bi(CF_3)_3$	–
$(3\text{-}FC_6H_4)_2BiCl$	8	79	$(3\text{-}FC_6H_4)_2Bi(CF_3)$	71
			$(3\text{-}FC_6H_4)Bi(CF_3)_2$	26
			$Bi(CF_3)_3$	3
$(4\text{-}FC_6H_4)_2BiCl$	8	84	$(4\text{-}FC_6H_4)_2Bi(CF_3)$	90
			$(4\text{-}FC_6H_4)Bi(CF_3)_2$	10
			$Bi(CF_3)_3$	–
$(4\text{-}CF_3C_6H_4)_2BiCl$	8	94	$(4\text{-}CF_3C_6H_4)_2Bi(CF_3)$	93
			$(4\text{-}CF_3C_6H_4)Bi(CF_3)_2$	3
			$Bi(CF_3)_3$	4

2.2. ^{19}F *NMR spectra of* $(R-C_6H_4)_{3-n}Bi(CF_3)_n$ *(n = 1 and 2) (Table 2)*

The resonances of the CF_3 groups of $(R-C_6H_4)Bi(CF_3)_2$ in $CDCl_3$ solution are located in the region between δ −34.8 and −36.2 ppm. No dependence of the chemical shift on the substituent of the phenyl group was observed. The same applies to the chemical shifts of $(R-C_6H_4)_2Bi(CF_3)$; here the resonances occur between δ −37.8 and −38.7 ppm. The $^1J(^{19}F-^{13}C)$ couplings have absolute values of 389 ± 1.8 Hz; the ^{13}C satellites of the bis(trifluoromethyl) derivatives are split into quartets with a $^4J(^{19}F-^{19}F)$

Table 2
^{19}F NMR data for $(R-C_6H_4)_{3-n}Bi(CF_3)_n$ ($n=1$ and 2) in $CDCl_3$ solution

Compound	$\delta[Bi(CF_3)]$ (ppm)	$^1J(^{19}F-^{13}C)$ (Hz)	$^4J(^{19}F-^{19}F)$ (Hz)	$^1\Delta(^{12/13}C-^{19}F)$ (ppm)	δ(substituent) (ppm)
$(C_6H_5)Bi(CF_3)_2$ [a]	−36.2	389.1	4.8	0.127	
$(4\text{-}CH_3C_6H_4)Bi(CF_3)_2$ [b]	−35.3	389.2	4.8	0.136	
$(3\text{-}FC_6H_4)Bi(CF_3)_2$	−34.8	387.5	4.8	0.142	−110.0
$(4\text{-}FC_6H_4)Bi(CF_3)_2$	−35.1	387.5	4.8	0.142	−109.0
$(4\text{-}CF_3C_6H_4)Bi(CF_3)_2$	−34.8	387.5	4.8	0.142	−63.7
$(C_6H_5)_2Bi(CF_3)$ [a]	−38.6	390.8		0.127	
$(4\text{-}CH_3C_6H_4)_2Bi(CF_3)$	−38.3	389.0		0.139	
$(3\text{-}FC_6H_4)_2Bi(CF_3)$	−37.8	387.3		0.141	−111.1
$(4\text{-}FC_6H_4)_2Bi(CF_3)$	−38.5	387.6		0.142	−111.3
$(4\text{-}CF_3C_6H_4)_2Bi(CF_3)$	−38.7	387.5		0.142	−63.5

[a] Solvent CH_3CN; taken from Ref. [4].
[b] Sample contained 15% $(4\text{-}CH_3C_6H_4)_2Bi(CF_3)$ as an impurity.

coupling of 4.8 Hz; all couplings are of the same order of magnitude as determined for $Bi(CF_3)_3$ [2].

$(R-C_6H_4)Bi(CF_3)_2$ may be regarded as aromatic compounds containing a $Bi(CF_3)_2$ substituent. To obtain quantitative estimates of the electronic effects of the $Bi(CF_3)_2$ substituent, the ^{19}F NMR spectra of $(3\text{-}FC_6H_4)Bi(CF_3)_2$ and $(4\text{-}FC_6H_4)Bi(CF_3)_2$ have been recorded in CCl_4 solution. The values σ_I, $\sigma_R{}^0$ and σ_P have been calculated from the Taft correlation equations [10,11]. The data obtained are summarized in Table 3. These data reveal that the effect of the $Bi(CF_3)_2$ substitutent is strongly inductive in character. The resonance effect is negligibly small. Similar small resonance effects have been observed for many compounds when the atom directly bonded to the aromatic system is an element of the fifth or sixth period (compare Table 3). The small $\sigma_R{}^0$ values for the $Bi(CF_3)_2$ substituent indicate that there is no noticeable electron-withdrawing effect due to d_π–p_π interactions between the π-orbitals of the aromatic system and the vacant metal d-orbitals. The total electron-withdrawing character σ_P can be compared with that of the NO_2 substituent ($\sigma_P=0.78$ [12]).

Table 3
Inductive and resonance parameters of the $Bi(CF_3)_2$ substituent and some related groups determined from the ^{19}F NMR shifts of the $3\text{-}FC_6H_4$ and $4\text{-}FC_6H_4$ groups using Taft's correlation equations [10,11]

Substituent	σ_I	$\sigma_R{}^0$	σ_P	Ref.
$-N(CF_3)_2$	0.49	0.01	0.50	[12]
$-P(CF_3)_2$	0.50	0.19	0.69	[12]
$-Bi(CF_3)_2$	0.80	0.03	0.83	
$-Sb(C_6H_5)_2$	0.20	−0.01	0.19	[13]
$-Bi(C_6H_5)_2$	0.22	−0.04	0.18	[13]
$-Hg(CF_3)$	0.27	0.05	0.32	[12]
$-I(OCOCH_3)_2$	0.85	0.06	0.91	[12]
$-I(OCOCF_3)_2$	1.00	0.05	1.05	[12]

2.3. *Reactions of $(C_6H_5)_{3-n}Bi(CF_3)_n$ (n = 0–3) with benzoylpyridinium chloride*

In a previous paper, we described the reactions of $Cd(CF_3)_2$ complexes with benzoyl chloride in the presence of pyridine [14]. These reactions yielded trifluoroacetophenone with considerable amounts of (trifluoromethyldihydropyridine)benzoyl amides, benzyl alcohols and benzoic acid benzyl esters. In another paper, we described our successful attempt to use $Bi(CF_3)_3$ as a selective CF_3 group-transfer reagent in the same system [2]. However, $(C_6H_5)_3Bi$ was successfully used as a phenylation reagent to transfer acid chlorides into the corresponding phenones in the presence of $Pd(OCOCH_3)_2/N(C_2H_5)_3$ [15], whereas the reactions of acetyl chloride with $(C_6H_5)_3Bi$ in the absence of any catalyst only yielded acetophenone in poor yield [16].

The reactions of $(C_6H_5)_3Bi$ and $Bi(CF_3)_3$ with benzoylpyridinium chloride proceed very selectively to give the corresponding phenone within 2 h in better than 65% yield (Table 4).

$$3C_6H_5COCl+3NC_5H_5 \longrightarrow 3[C_6H_5CO-NC_5H_5]^+\ Cl^- \quad (7)$$

Table 4
Products and yields of the reactions of $(C_6H_5)_{3-n}Bi(CF_3)_n$ ($n=1$–3) with benzoylpyridinium chloride

Compound	Products	Isolated yields [a] (%)
$(C_6H_5)_3Bi$	$C_6H_5COC_6H_5$	65
$(C_6H_5)_2Bi(CF_3)$	$C_6H_5COC_6H_5$	61
	$C_6H_5COCF_3$	trace
$(C_6H_5)Bi(CF_3)_2$	$C_6H_5COC_6H_5$	55
	$C_6H_5COCF_3$	12
$Bi(CF_3)_3$	$C_6H_5COCF_3$	69

[a] Relative to $[C_6H_5CONC_5H_5]^+\ Cl^-$.

$$3[C_6H_5CO-NC_5H_5]^+\ Cl^- + R_3Bi \longrightarrow 3C_6H_5COR + BiCl_3 + 3NC_5H_5 \quad (8)$$

$(R = C_6H_5, CF_3)$

As expected from the redistribution equilibria, the reactions of the mixed derivatives $(C_6H_5)_2Bi(CF_3)$ and $(C_6H_5)Bi(CF_3)_2$ did not give uniform products. In the case of the diphenyl derivative, mainly benzophenone besides traces of trifluoroacetophenone were formed; reactions with the monophenyl derivative gave a 5:1 product mixture of $C_6H_5COC_6H_5$ and $C_6H_5COCF_3$. However, in all cases by-products as observed during the reactions of benzoyl chloride with $Cd(CF_3)_2$ complexes [14] were not formed.

3. Experimental details

Literature methods were used for the syntheses of $(4\text{-}CH_3C_6H_4)_3Bi$ [17], $(4\text{-}CF_3C_6H_4)_3Bi$ by analogy to $(4\text{-}CH_3C_6H_4)_3Bi$ [17], $(3\text{-}FC_6H_4)_3Bi$ [18], $(4\text{-}FC_6H_4)_3Bi$ [18], $Cd(CF_3)_2 \cdot 2CH_3CN$ [19], $Bi(CF_3)_3$ [2,20], $BiBr_3$ [21]. All solvents were purified by common methods [22]. $(C_6H_5)_3Bi$ (Riedel-de Haën, Seelze (Germany)) and $BiCl_3$ (Riedel-de Haën, Seelze (Germany)) were used as received. C_6H_5COCl was used after treatment with $SOCl_2$.

The arylbismuth halides were prepared according to Ref. [7] in diethyl ether solution and obtained in quantitative yields. Any visible decomposition or melting points and NMR data are summarized in Table 5. The ^1H NMR data for $(4\text{-}CH_3C_6H_4)BiBr_2$ and $(4\text{-}CH_3C_6H_4)_2BiCl$ in DMSO-d_6 solution are identical with those given in Ref. [23]. All compounds were handled in a dry N_2 atmosphere using Schlenk techniques.

The ^{19}F NMR spectra were recorded on a Bruker model WP-200 spectrometer (^{19}F, 188.3 MHz) or on a Bruker model AC-200 spectrometer, the ^1H NMR spectra on a Gemini 200 spectrometer with positive shifts being lowfield from the standards external CCl_3F (^{19}F) and internal $[(CH_3)_3Si]_2O$ (^1H).

3.1. Synthesis of $(R-C_6H_4)Bi(CF_3)_2$

To a solution consisting of 1.0 mmol of $(R-C_6H_4)BiBr_2$ in 5 ml of CH_3CN was added 2.2 mmol of $Cd(CF_3)_2 \cdot 2CH_3CN$. The mixture was stirred at ambient temperature. The reaction times are listed in Table 1. CH_3OH (1 ml) was added to the mixture to destroy excess $Cd(CF_3)_2 \cdot 2CH_3CN$ and $Cd(CF_3)Br \cdot 2CH_3CN$. The precipitate was filtered and the solvent distilled off in vacuo. A colourless oily liquid remained. The composition of the oil was determined by ^{19}F NMR spectroscopy. Fractional distillation of the crude product at 1×10^{-3} hPa gave the pure compound. $(4\text{-}CH_3C_6H_4)Bi(CF_3)_2$ could not be obtained as a pure compound but always contained 15% of $(4\text{-}CH_3C_6H_4)_2Bi(CF_3)$. Storage of pure $(R-C_6H_4)Bi(CF_3)_2$ or as an acetonitrile solution for several days led to dismutation into $(R-C_6H_4)_2Bi(CF_3)$, $Bi(CF_3)_3$ and $(R-C_6H_4)_3Bi$. Fluorine analysis for $(3\text{-}FC_6H_4)Bi(CF_3)_2$: [Found (Calculated)]: F, 29.86% (30.09%). Elemental analysis for $(4\text{-}FC_6H_4)Bi(CF_3)_2$: [Found (Calculated)]: C, 22.12% (21.71%); H, 2.05% (1.54%); F, 29.79% (30.09%). Elemental analysis for $(4\text{-}CF_3C_6H_4)Bi(CF_3)_2$: [Found (Calculated)]: C, 22.28% (21.95%); H, 1.20% (0.81%); F, 33.22% (34.75%).

3.2. Synthesis of $(R-C_6H_4)_2Bi(CF_3)$

To 1.0 mmol of $(R-C_6H_4)_2BiCl$ dissolved in 5 ml of CH_3CN was added 1.1 mmol of $Cd(CF_3)_2 \cdot 2CH_3CN$. The further procedures were as given above. Elemental analysis for $(3\text{-}FC_6H_4)_2Bi(CF_3)$: [Found (Calculated)]: C, 33.68% (33.33%); H, 1.98% (1.70%); F, 20.80% (20.29%). Elemental analysis for $(4\text{-}FC_6H_4)_2Bi(CF_3)$: [Found (Calculated)]: C, 33.11% (33.33%); H, 2.23% (1.70%); F, 19.98% (20.29%). Elemental analysis for $(4\text{-}CF_3C_6H_4)_2Bi(CF_3)$: [Found (Calculated)]: C, 32.01% (31.69%); H, 1.40% (1.89%); F, 29.55% (30.10%).

3.3. Reactions of $(C_6H_5)_{3-n}Bi(CF_3)_n$ $(n = 0–3)$ with benzoylpyridinium chloride

To a solution consisting of 1.40 g (10 mmol) of C_6H_5COCl in 30 ml of n-pentane at −30 °C was added

Table 5
Melting points and ^{19}F NMR and ^1H NMR data for $(R-C_6H_4)_{3-n}BiX_n$ ($n = 1$ and 2; X = Cl, Br) (solvent $(CD_3)_2SO$)

Compound	M.p. (°C)	$\delta(^{19}F)$ (ppm)	δ(2-H) (ppm)	δ(3-H) (ppm)	δ(4-H) (ppm)	δ(5-H) (ppm)	δ(6-H) (ppm)
$(3\text{-}FC_6H_4)BiBr_2$	203–205 (dec.)	−112.2	8.82		7.94	7.08	9.00
$(4\text{-}FC_6H_4)BiBr_2$	230 (dec.)	−111.6	9.04	7.51		7.51	9.04
$(4\text{-}CF_3C_6H_4)BiBr_2$	192–195 (dec.)	−60.8	9.25	8.08		8.08	9.25
$(3\text{-}FC_6H_4)_2BiCl$	118–119	−112.2	8.09		7.64	7.05	8.16
$(4\text{-}FC_6H_4)_2BiCl$	129–130	−112.7	8.26	7.31		7.31	8.26
$(4\text{-}CF_3C_6H_4)_2BiCl$	185–187	−60.6	8.50	7.85		7.85	8.50

0.81 ml (10 mmol) of pyridine in a dropwise manner. After 10 min, the solvent was distilled off in vacuo at -10 °C; white benzoylpyridinium chloride remained. The salt was dissolved in 10 ml of CH_3CN and 15 mmol of the corresponding bismuth derivative was added. The reaction mixture was stirred for 2 h at ambient temperature. All volatile products were distilled off under reduced pressure. Benzophenone was extracted from the residue with diethyl ether; the ether solution was washed with water and dried over $MgSO_4$. Benzophenone was identified by its melting point of 49–51 °C. From the distillate, trifluoroacetophenone was obtained by distillation at normal pressure and identified by its boiling point (165–166 °C) and ^{19}F NMR spectrum ($\delta(CDCl_3)$ -72.1 ± 0.2 ppm [14]). The yields are given in Table 4.

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