6864 *Organometallics* **2007,** *26,* 6864–6866

Notes

A New Methodology for Synthesis of Aryl Bismuth Compounds: Arylation of Bismuth(III) Carboxylates by Sodium Tetraarylborate Salts

Vitalie Stavila, John H. Thurston, Darío Prieto-Centurión, and Kenton H. Whitmire*

Department of Chemistry, MS 60, Rice University, 6100 Main Street, Houston, Texas 77005

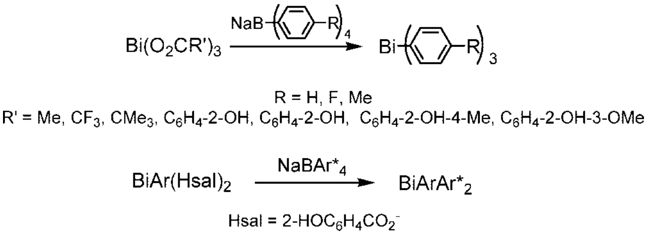
Received September 28, 2007

Summary: Sodium tetraarylborate salts $Na[BAr_4]$ *(*$Ar = C_6H_5$ *(Ph),* C_6H_4*-Me-4 (tolyl),* C_6H_4*-F-4) are found to be efficient arylating species for a range of bismuth(III) aromatic and aliphatic carboxylates including* $Bi(Hsal^*)_3$ *(*$Hsal^* =$ *2-HO-*$C_6H_4CO_2^-$ *(Hsal); 4-Me-2-HO-*$C_6H_3CO_2^-$ *(*$Hsal^{4Me}$*); or 3-MeO-2-HO-*$C_6H_3CO_2^-$ *(*$Hsal^{3OMe}$*)) and* $Bi(O_2CR)_3$ *(R = Me,* CMe_3*, and* CF_3*) to produce triaryl bismuth compounds. The reactions may be carried out in ethanol, tetrahydrofuran, or acetone. The arylbismuth bis(salicylates)* $BiPh(Hsal)_2$ *and* $Bi(tolyl)(Hsal)_2$ *exhibit similar reactivity in refluxing THF and may be used to produce mixed arylbismuthines* $BiPh_x(tolyl)_{3-x}$*. Formation of the known arylbismuth compounds was confirmed by IR spectroscopy, X-ray crystallography, NMR spectroscopy (*^1H*,* ^{11}B*,* ^{13}C*, and* ^{19}F*), and mass spectrometry. This is a facile synthesis of both symmetrical and unsymmetrical triarylbismuthines involving the aryl group transfer from the tetraarylborate ions to bismuth(III) under mild conditions.*

Introduction

Aryl bismuth compounds have been known since the 1880s, when Michaelis reported the synthesis of triphenyl bismuth from Bi−Na alloys and bromobenzene in ethylacetate.[1,2] The chemistry and uses of arylbismuth compounds have been recently reviewed.[3] They are employed as co-catalysts for various polymerization processes, as additives in dental and medical devices as X-ray opaque substances, and as arylating agents for a range of organic substrates. They serve as starting compounds to synthesize various classes of bismuth(III) and bismuth(V) compounds, and even though the coordinating ability of bismuth(III) is weak, some examples of their use as ligands for transition metals have been reported. Triarylbismuth(III) derivatives are usually prepared from $BiCl_3$ using organomagnesium or organolithium reagents in donor solvents such as THF or diethyl ether. This methodology is well-developed, but the reactions must be run under a rigorously dry atmosphere and one must carefully control the rate of addition of the reagents and the temperature. $BiCl_3$, which is hygroscopic and must be carefully purified prior to use, undergoes redistribution reactions with $BiAr_3$ to give mixtures of $BiAr_{3-x}Cl_x$ ($x = 0$–3), so the stoichiometry must be precisely controlled in order to achieve good yields of pure materials.

Scheme 1. Synthetic Procedures to Triarylbismuth Compounds by Arylation with Sodium Tetraarylborates



The use of tetraarylborate salts as nucleophilic arylating agents for metal ions has been reported.[4] A number of main group and transition metals undergo arylation upon treatment with tetraarylborate salts. During our investigations of heterometallic complexes as precursors for mixed-metal oxide materials, we found that salicylate-alkoxide complexes can be produced from the reaction of bismuth(III) salicylate with early transition metal alkoxides. In an attempt to introduce alkali metal cations in the system, some heterometallic Bi−Nb and Bi−Ta complexes were treated with sodium tetraphenylborate. The products contained no sodium; however, one or more salicylate ions on bismuth were replaced by phenyl groups. These results, which will be detailed elsewhere, prompted us to explore the general reactivity of tetraarylborate salts toward bismuth(III) carboxylates.

Results and Discussion

Symmetrical tris(aryl)bismuth compounds are prepared by the reaction of bismuth(III) salicylates with sodium tetraaryl borates (Scheme 1). The reactions proceed smoothly in good to excellent yields in THF, alcohols, or acetone. In a representative procedure, freshly prepared $Bi(Hsal)_3$ reacts with 3 equiv of sodium tetraphenylborate in ethanol at room temperature over a period of 16 h, during which the initial pale orange color of the reaction mixture gradually changes to pale yellow. Upon

---

* To whom correspondence should be addressed. E-mail: whitmir@rice.edu. Phone: 713-348-5650. Fax: 713-348-5155.

(1) Michaelis, A.; Polis, A. *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 55–56.

(2) Michaelis, A.; Marquardt, A. *Liebigs Ann. Chem.* **1889**, *251*, 323–335.

(3) (a) Suzuki, H., Matano, Y., Eds. *Organobismuth Chemistry*; Elsevier: New York, 2001; 619 pp. (b) Freedman, L. D.; Doak, G. O. *Chem. Rev.* **1982**, *82*, 15–57.

(4) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927–942.

(5) (a) Coombs, D. L.; Aldridge, S.; Rossin, A.; Jones, C.; Willock, D. J. *Organometallics* **2004**, *23*, 2911–2926. (b) Sacconi, L.; Dapporto, P.; Stoppioni, P. *Inorg. Chem.* **1976**, *15*, 325–329. (c) Haines, R. J.; Du Preez, A. L. *J. Am. Chem. Soc.* **1971**, *93*, 2820–2821.

10.1021/om7009667 CCC: $37.00

the removal of solvent, the product was extracted into hexanes and subjected to column filtration to produce $BiPh_3$ in 72% yield. Reaction of Na[B(tolyl)$_4$] and Bi(Hsal)$_3$ proceeded similarly. The introduction of a methyl or methoxy substituent on the salicylate moiety did not have a significant effect on the reaction. Since the method of preparation of the bismuth salicylates may affect their solubilities (those prepared in refluxing toluene often exhibit a lower solubility than those prepared from a solventless reaction),[6] the method of preparation of the bismuth salicylate was also found to have very little effect on the yield of the aryl bismuth products.

A drawback to the procedure described above is that $BiPh_3$ was the reagent used to prepare the bismuth carboxylates. To develop a useful synthetic methodology, we explored using bismuth(III) carboxylates prepared from inexpensive, commercially available inorganic reagents such as Bi_2O_3 or $(BiO)_2CO_3$ as alternative starting materials. For this study, bismuth(III) acetate, pivalate, and trifluoroacetate were prepared from the reaction of Bi_2O_3 with the appropriate carboxylic acids in the presence of their anhydrides, the latter being added to scavenge the water produced as a byproduct of the reaction. After the removal of all volatiles, the carboxylates were suspended in THF without further purification and treated with the appropriate tetraarylborate salt. The reactions proceeded in high yield within a short time with $Bi(O_2CCMe_3)_3$ or $Bi(O_2CCF_3)_3$. In the case of $Bi(OAc)_3$ (OAc = acetate) lower yields were obtained even at prolonged reaction times, which we attribute to the lower solubility of this compound. When employing a 1:1 mixture of Na[BPh_4] and Na[B(tolyl)$_4$] with either Bi(Hsal)$_3$ or $Bi(O_2CCF_3)_3$, an approximately statistical mixture of $BiPh_{3-x}$(tolyl)$_x$ (x = 0–3) resulted. This mixture is difficult to separate, but a rational approach to asymmetrically substituted compounds is available starting with $ArBi(OC_2R)_2$. Such unsymmetrical organobismuth compounds were obtained by treating BiAr(Hsal*)$_2$[7] with 2 equiv of Na[BAr*$_4$] (Scheme 1) in yields of about 70%.

The use of fluorinated sodium tetraarylborates was also examined, since these reagents are expected to be less nucleophilic than the phenyl or tolyl salts. Use of sodium tetrakis(4-fluorophenyl)borate produced $Bi(C_6H_4\text{-}4\text{-}F)_3$, but the product was slightly less pure than the phenyl and tolyl derivatives, apparently contaminated with traces of $B(C_6H_4\text{-}4\text{-}F)_3$, as evidenced by the ^1H NMR spectrum. This product, however, still gave a sharp melting point close to the literature value.

In some of the reported aryl transfer reactions from tetraarylborate salts to metal centers,[5] BPh_3 was detected as a byproduct. In our case, however, BPh_3 was not detected. It is known that BPh_3 can react even with low levels of oxygen and water to produce a wide range of decomposition products, including tetraphenyldiboroxane and phenylboronic acids. In the reaction with Ar = C_6H_4-F-4, NMR data indicated the presence of $B(C_6H_4\text{-}F\text{-}4)_3$, so we assume that BAr_3 is formed in each reaction, and this hypothesis is consistent with the observed 3:1 stoichiometry. The use of only one aryl group on the borate salt is a limitation of the reaction, so we explored the possibility of using arylboronic acids, $ArB(OH)_2$, in place of Na[BAr_4]. It is known that lead(IV) carboxylates may undergo aryl transfer reactions with aryl boronic acids; however only traces of $BiAr_3$ were detected in our case.

Table 1. Arylation of Bismuth(III) Carboxylates by Na[BAr$_4$] to Give BiAr$_3$[a]

entry	Bi(III) carboxylate	Ar	solvent	temp	time (h)	yield (%)
1	Bi(Hsal)$_3$ sol.	Ph	EtOH	rt	16	72
2	Bi(Hsal)$_3$ sol.	tolyl	EtOH	rt	16	70
3	Bi(Hsal)$_3$ sol.	Ph	THF	rt	16	71
4	Bi(Hsal^{4Me})$_3$ sol.	Ph	THF	rt	16	65
5	Bi(Hsal^{3OMe})$_3$ sol.	Ph	THF	rt	16	62
6	Bi(Hsal)$_3$ s/s	Ph	THF	rt	16	75
7	Bi(Hsal)$_3$ s/s	Ph	THF	reflux	16	83
8	Bi(Hsal)$_3$ s/s	Ph	THF	reflux	4	80
9	Bi(Hsal)$_3$ s/s	tolyl	THF	rt	16	73
10	Bi(Hsal)$_3$ s/s	tolyl	THF	reflux	16	82
11	Bi(Hsal)$_3$ s/s	C_6H_4-F-4	THF	reflux	16	56
12	Bi(Hsal)$_3$ s/s	Ph	Me_2CO	rt	4	58
13	Bi(Hsal)$_3$ s/s	Ph	Me_2CO	rt	16	64
14	Bi(Hsal^{4Me})$_3$ s/s	Ph	THF	rt	16	74
15	Bi(Hsal^{3OMe})$_3$ s/s	Ph	THF	rt	16	69
16	Bi(Hsal^{4Me})$_3$ s/s	tolyl	THF	reflux	16	72
17	Bi(Hsal^{3OMe})$_3$ s/s	tolyl	THF	reflux	16	69
18	$Bi(O_2CCF_3)_3$	Ph	THF	reflux	16	81
19	$Bi(O_2CCF_3)_3$	Ph	THF	reflux	4	77
20	$Bi(O_2CMe)_3$	Ph	THF	rt	4	25
21	$Bi(O_2CMe)_3$	Ph	THF	reflux	16	54
22	$Bi(O_2CMe)_3$	Ph	THF	reflux	48	58
23	$Bi(O_2CCMe_3)_3$	Ph	THF	reflux	16	70
24	$Bi(O_2CCF_3)_3$	tolyl	THF	reflux	16	84
25	$Bi(O_2CCF_3)_3$	C_6H_4-F-4	THF	reflux	16	60

[a] The products were identified by their IR, ^1H and ^{13}C NMR, and mass spectra and, in the case of Bi(tolyl)$_3$, by X-ray crystallography (see Supporting Information). The MALDI mass spectra of the products of the reactions in positive mode resulted in a number of ion fragments including those attributed to the oxo-species $[Bi_2O(Ar)_5]^+$ (m/z 819.14, calc for Ar = Ph 819.15, and m/z 889.23, calc for Ar = tolyl 889.23; see Supporting Information). sol. = prepared in refluxing toluene; s/s = prepared by a solid-state reaction at 130 °C; rt = room temperature.

Conclusions

A new arylation reaction of bismuth(III) carboxylates by using tetraarylborate salts has been developed. Both Na[BPh_4] and Na[B(tolyl)$_4$] are suitable reagents, producing $BiPh_3$ and Bi(tolyl)$_3$ from a range of bismuth(III) carboxylates. Particularly good results were obtained in THF at room temperature or at reflux. The reaction works best when using soluble bismuth(III) carboxylates, such as $Bi(O_2CCF_3)_3$. Under these conditions, the reactions go to completion in approximately 16 h with yields on the order of 70–80%. A potentially useful feature of this methodology is the production of unsymmetrical triarylbismuthines obtained by reacting $ArBi(O_2CR)_2$ with sodium tetrarylborates. These mild reactions are suitable for the preparation of various arylbismuth compounds and avoid the use of bismuth(III) chloride, a hygroscopic compound that undergoes facile redistribution reactions with triaryl bismuth compounds. Advantages of this synthetic procedure include (i) bismuth(III) carboxylates may serve as a source for Bi(III) and are easily prepared from inexpensive, common reagents such as bismuth(III) oxide or hydroxide; (ii) the reaction occurs under mild conditions in a range of organic solvents, both at room temperature and at reflux; (iii) the reaction is far less sensitive to oxygen and moisture than methods employing Grignard or organolithium reagents, and (iv) the reaction offers a convenient method of preparing unsymmetrically substituted triaryl bismuth complexes.

---

[6] (a) Andrews, P. C.; Deacon, G. B.; Jackson, W. R.; Maguire, M.; Scott, N. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 4634–4638. (b) Urano, M.; Wada, S.; Suzuki, H. *Chem. Commun.* **2003**, 1202–1203.

[7] Stavila, V.; Fettinger, J. C.; Whitmire, K. H. *Organometallics* **2007**, *26*, 3321–3328.

Experimental Section

General Information. All of the manipulations were carried out under a dry dinitrogen or argon atmosphere using standard Schlenk and glovebox techniques. Acetone was dried over Drierite and distilled over freshly activated molecular sieves. Ethanol, toluene, and tetrahydrofuran were distilled under dinitrogen from magnesium ethoxide, sodium, and sodium benzophenone ketyl, respectively. All reagents and chemicals, unless otherwise stated, were purchased from commercial sources. Commercial $BiPh_3$, H_2sal, H_2sal^{4Me}, and H_2Sal^{3OMe} were dried for 4 h *in vacuo* then transferred to a drybox. $Bi(Hsal)_3$, $Bi(Hsal^{4Me})_3$, and $Bi(Hsal^{3OMe})_3$ were prepared in refluxing toluene[8] or using the solid-state reaction of $BiPh_3$ with the corresponding acids.[6a] $BiPh(Hsal)_2$ and $Bi(tolyl)(Hsal)_2$ were prepared as described in the literature.[7] Sodium tetra(*p*-tolyl)borate was prepared by a slightly modified procedure reported by Wittig.[9]

Instrumentation. NMR spectra were recorded at room temperature in $CDCl_3$, CD_2Cl_2, C_6D_6, and d_6-acetone (containing 0.5% TMS) on Bruker Avance 400 and 500 spectrometers, and the ^1H and ^{13}C chemical shifts are reported relative to the shift of tetramethylsilane (TMS). ^{11}B and ^{19}F NMR spectra were referenced to external $BF_3 \cdot Et_2O$ and $CFCl_3$, respectively. Mass spectra were acquired using a Reflex IV (BrukerDaltonics Inc., Billerica, MA) matrix-assisted laser desorption ionization (MALDI) time-of-flight instrument equipped with pulsed ion extraction and a pulsed nitrogen laser (337 nm). IR spectra were recorded on a Nicolet 670 FT-IR spectrometer using attenuated total reflectance. Melting points were obtained in sealed capillaries on an Electrothermal melting point instrument and are uncorrected. Characterization data for all products are provided in the Supporting Information.

General Procedure for Synthesis of Triarylbismuthines by Tetraarylborate Salts. A solution of the appropriate sodium tetraarylborate (0.75 mmol) in 10 mL of indicated solvent (Table 1) was added dropwise at room temperature to a stirred solution or suspension of the bismuth(III) carboxylate (0.25 mmol) in 20 mL of the same solvent. The resulting mixture was refluxed and stirred for 16 h to complete the reaction. After the removal of the solvent under reduced pressure, the crude product was extracted into hexanes. The solution was filtered and subjected to column chromatography on silica gel (eluent: pentane/CH_2Cl_2, 90:10) to produce the corresponding triarylbismuthine.

General Procedure for Synthesis of Unsymmetrically Substituted Triaryl-Bismuth Compounds from Arylbismuth Dicarboxylates. The sodium tetraarylborate (0.4 mmol) in 10 mL of THF was added to a stirred solution of $ArBi(Hsal)_2$ (Ar = Ph, tolyl) (0.2 mmol) in THF (10 mL) at room temperature. The mixture was heated gradually and maintained at reflux overnight. After the THF was removed *in vacuo*, hexanes (20 mL) were added to the reaction mixture, which was then stirred for 30 min. After filtering, the compound was purified by column filtration on silica gel (eluent: pentane/CH_2Cl_2, 90:10) to produce the corresponding unsymmetrically substituted triarylbismuthine. The yields of $BiPh(tolyl)_2$ and $BiPh_2(tolyl)$ were 71% and 68%, respectively.

Acknowledgment. The Robert A. Welch Foundation is acknowledged for financial support. V.S. is grateful to NSF and NATO (DGE-0411679) for a postdoctoral fellowship. Dr. Larry Alemany and Dr. Sandy Yates are gratefully acknowledged for help with the NMR and mass spectrometric investigations, respectively.

Supporting Information Available: Analytical data for all products and CIF file giving crystallographic data for $Bi(tolyl)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7009667

---

(8) Thurston, J. H.; Whitmire, K. H. *Inorg. Chem.* **2002**, *41*, 4194.

(9) Wittig, G.; Raff, P. *Liebigs Ann. Chem.* **1951**, *573*, 195.