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# Synthesis and Reactions of Some Crowded Triorganylbismuthines

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**Synopsis.** Bismuth trichloride reacts smoothly with mesityl- and 2,4,6-triisopropylphenylmagnesium bromides in boiling tetrahydrofuran to form the corresponding triarylbismuthines in good yields, while a similar reaction with 2,4,6-triisopropylphenylmagnesium bromide halts at diarylation stage, giving chlorobis(2,4,6-triisopropylphenyl)bismuthine as the sole product. Several crowded alkyl-, alkenyl-, and alkynyldiarylbismuthines have been prepared from the above diarylchlorobismuthine through the reaction with an appropriate organolithium reagent.

In connection with our ongoing program on organobismuth chemistry, it became necessary for us to know how far the bulky aryl groups can be introduced directly onto the trivalent bismuth atom by the conventional procedures, i.e., by the reaction of a Grignard or organolithium reagent with bismuth trichloride ($BiCl_3$). As the bulky aryl ligand, we chose four different 2,4,6-trisubstituted phenyl groups of increasing steric demand; 2,4,6-trimethylphenyl (mesityl), 2,4,6-triethylphenyl, 2,4,6-triisopropylphenyl, and 2,4,6-tri-*t*-butylphenyl groups.

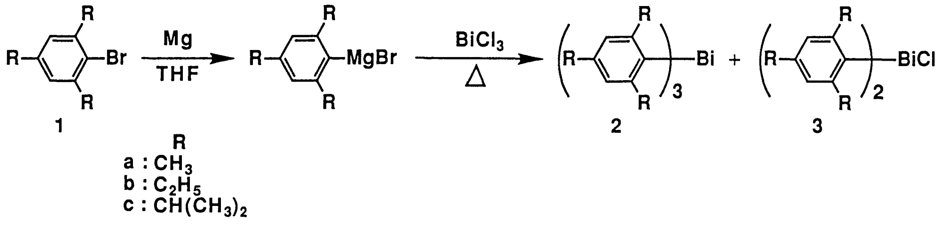
1,3,5-Trialkyl-2-bromobenzenes (**1a**—**c**) were converted into the corresponding Grignard reagent and treated with one third mole equiv of $BiCl_3$. Trimesitylbismuthine (**2a**)¹⁾ and tris(2,4,6-triethylphenyl)bismuthine (**2b**) were obtained as a crystalline solid in good yields. In contrast to the reaction of phenylmagnesium bromide with $BiCl_3$ which readily takes place at salt–ice bath temperature, heating under reflux was necessary to complete the conversion into **2a** and **2b**. Recently, tris[2,4,6-(trifluoromethyl)phenyl]bismuthine was obtained by Whitmire and co-workers as an example of sterically crowded bismuthines.²⁾ This compound undergoes facile oxidative and hydrolytic decompositions upon exposure to air, while compounds **2a** and **2b** are comparatively stable in a solid state.³⁾ In view of a similarity in steric bulkiness around the bismuth atom, the presence of electron-withdrawing groups on the aromatic ring appears to enhance the lability of triarylbismuthines to oxidative degradation (Scheme 1).

Attempts to obtain tris(2,4,6-triisopropylphenyl)bismuthine (**2c**) were not successful; prolonged heating under reflux of $BiCl_3$ with an excess of 2,4,6-triisopropylphenylmagnesium bromide in tetrahydrofuran (THF) only led to chlorobis(2,4,6-triisopropylphenyl)bismuthine (**3c**), no triarylated bismuth compound being formed.⁴⁾ The chloride **3c** was obtained almost quantitatively by the reaction of the Grignard reagent with one half mole equiv of $BiCl_3$ at ambient temperature. Combined steric effect of the two bulky aryl moieties apparently prevented further attack of the Grignard reagent on the bismuth atom. Different from ordinary chlorodiarylbismuthines which are quite sensitive to moisture, the compound **3c** is stable enough to be eluted from silica gel column without hydrolytic decomposition. It is easily soluble in common organic solvents and can be stored in a solid state over days without decomposition.

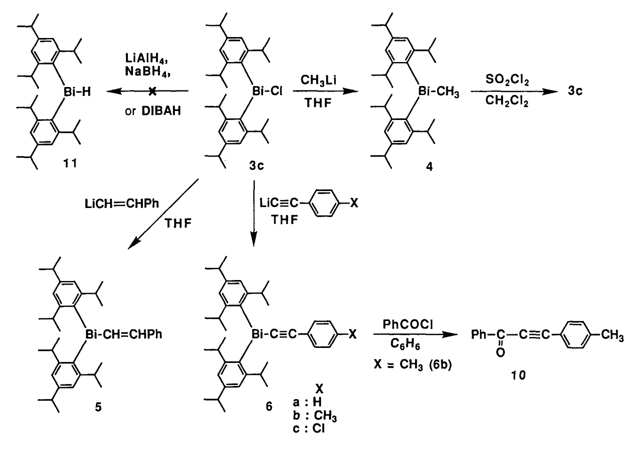
Because of the difficulty in obtaining the Grignard reagent, 2-bromo-1,3,5-tri-*t*-butylbenzene (**1d**) was converted into the lithium reagent by the halogen–metal exchange with butyllithium in THF and then treated with $BiCl_3$. The reaction mixture showed a characteristic color change from deep orange to pale yellow, forming some powdery precipitates, but after aqueous workup 1,3,5-tri-*t*-butylbenzene was isolated as the main product.

The compound **3c** reacted with methyllithium at −78 °C to afford bis(2,4,6-triisopropylpheny)methylbismuthine (**4**) as colorless crystals. This compound is stable in a solid state and dose not show any sign of degradation in open air. Alkyldiphenylbismuthines were first synthesized by Kaufmann in 1980 by the reaction of chlorodiphenylbismuthine with alkyllithiums.⁵⁾ These unsymmetrical bismuthines are air-sensitive liquids which need to be stored under the exclusion of light and air. Steric bulkiness arising from two 2,4,6-triisopropylphenyl groups would contribute greatly to the protection of the labile Bi–alkyl bond in **4** and the Bi–Cl bond in **3c**. Due to the enhanced lipophilicity by six isopropyl groups, the compound **4** is highly soluble in nonpolar solvents such as pentane and hexane.

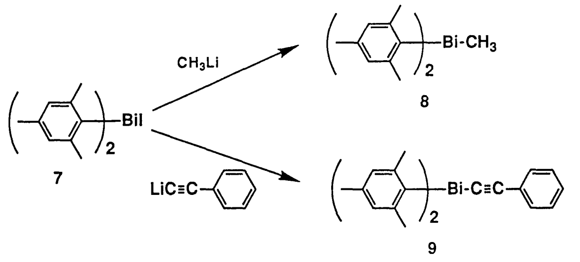
Crowded alkenyl- and alkynyldiarylbismuthines (**5** and **6a**—**c**) were prepared in moderate yields by treatment of **3c** with the respective alkenyl- and alkynyllithiums. These mixed triorganylbismuthines are also air-stable crystalline solids and readily soluble in nonpolar solvents. By similar reactions of iododimesitylbismuthine (**7**) with the corresponding lithium reagents, dimesitylmethylbismuthine (**8**)⁶⁾ and dimesityl(2-phenylethynyl)bismuthine (**9**) were obtained both as stable



Scheme 1.



Scheme 2.



Scheme 3.

crystalline solids. Alkynyldiarylbismuthines were prepared for the first time by Hartmann and co-workers in 1962,[7] but to our knowledge alkenyldiarylbismuthines are not previously described.

Unsymmetrical bismuthine **4** easily suffered chlorinolysis with sulfuryl chloride at −40 °C. Bond cleavage occurred exclusively at the Bi–$C_{sp^3}$ position to form **3c** and methyl chloride. The reaction probably proceeded through the intermediary of a bismuth(V) compound, which underwent the reductive elimination of methyl chloride to yield **3c** as the preferential product. Trialkylbismuth dichlorides are known to be unstable and rapidly decompose into dialkylchlorobismuthines and alkyl chlorides.[8] When compound **6b** was heated with benzoyl chloride in benzene for several hours, the chlorinative cleavage of a Bi–$C_{sp}$ bond and the acylation of an acetylenic carbon atom occurred simultaneously to give 3-(4-methylphenyl)-1-phenyl-2-propyn-1-one (**10**) and **3c** in 51 and 65% isolated yields, respectively. Under similar conditions bismuthines **4** and **5** were appreciably stable toward the action of acid chloride and slowly decomposed to unidentified products.

Attractive attempts to obtain bis(2,4,6-triisopropylphenyl)bismuthine (**11**), the first diarylbismuthine,[9] by the reduction of **3c** with lithium aluminum hydride, sodium borohydride or diisobutylaluminum hydride (DIBAH) were all unsuccessful. In every case, 1,3,5-triisopropylbenzene and a black inorganic substance were obtained instead of the expected diarylbismuthine **11**.

## Experimental

Mps were measured on a Yanagimoto hot-stage apparatus and are uncorrected. $^1$H NMR spectra were obtained in $CDCl_3$ at 200 MHz using a Varian Gemini 200 spectrometer, with tetramethylsilane as an internal standard. IR spectra were recorded with a Shimadzu FTIR-8100S spectrometer as potassium bromide pellets. EI mass spectra were determined with a Shimadzu GCMS-QP 2000A mass spectrometer. Column chromatography was performed on silica gel (Wakogel C-200) using a hexane–ethyl acetate mixture as an eluent. 1,3,5-Trialkyl-2-bromobenzenes were prepared from the corresponding hydrocarbons according to the reported procedure.[10] Tetrahydrofuran (THF) and benzene were distilled from calcium hydride or sodium metal under an argon atmosphere prior to use. Magnesium metal and methyllithium were used as received. Commercial bismuth trichloride was purified by heating with thionyl chloride under reflux prior to use.

**Tris(2,4,6-trialkylphenyl)bismuthines (2a and 2b). General Procedure:** To a freshly prepared THF (40 ml) solution of 2,4,6-trialkylphenylmagnesium bromide (30 mmol) was added $BiCl_3$ (2.84 g, 9 mmol) at 0 °C. After stirring for a suitable hour (4 h for **2a** and 6 h for **2b**) at 50—60 °C, the suspension was filtered through a Celite bed. The filtrate was poured into ice-water (50 ml) and the aqueous phase was extracted with ethyl acetate (20 ml×2). The combined extracts were evaporated under reduced pressure to afford a pale yellow gummy substance, which was recrystallized from hexane/ether or pentane/ether. Yield, 70—90%.

**Trimesitylbismuthine (2a).** Pale yellow needles (hexane–ether). Mp 136—138 °C (lit, 134—135 °C).[1] $^1$H NMR $\delta$=2.23 (9H, s), 2.28 (18H, s), 6.94 (6H, s); MS (70 eV) *m/z* 566 ($M^+$), 447, 327, 237, 209, 119, 105, 91; IR 3010, 1595, 1560, 1440, 1290, 1020, 1000, 845, 700 cm$^{-1}$. Found: C, 57.33; H, 6.03%. Calcd for $C_{27}H_{33}Bi$: C, 57.24; H, 5.87%.

**Tris(2,4,6-triethylphenyl)bismuthine (2b).** Pale yellow crystals (pentane–ether). Mp 82—84 °C. $^1$H NMR $\delta$=0.98 (18H, t, $J$=7.1 Hz), 1.21 (9H, t, $J$=7.4 Hz), 2.66 (12H, q, $J$=7.1 Hz and 6H, q, $J$=7.4 Hz), 6.98 (6H, s) ; MS (70 eV) *m/z* 692 ($M^+$), 531, 369, 291, 277, 263, 209, 161, 133, 105; IR 2874, 1603, 1557, 1412, 1316, 1264, 1073, 999, 866, 708 cm$^{-1}$. Found: C, 62.11; H, 7.36%. Calcd for $C_{36}H_{51}Bi$: C, 62.41; H, 7.42%.

**Chlorobis(2,4,6-triisopropylphenyl)bismuthine (3c):** To a freshly prepared THF (30 ml) solution of 2,4,6-triisopropylphenylmagnesium bromide (31 mmol) was added an ethereal solution (10 ml) of $BiCl_3$ (4.20 g, 13.3 mmol) at 0 °C. After stirring for 6 h at room temperature, the reaction mixture was filtered through a Celite bed. Removal of the solvent from the filtrate, extraction of the solid residue with benzene, and evaporation of the solvent left a yellow sticky oil, which was chromatographed over a silica-gel column using hexane/benzene as an eluent to give **3c** (7.80 g, 90%). Yellow crystals (hexane–ether). Mp 130—132 °C. $^1$H NMR $\delta$=1.06 (12H, d, $J$=7.0 Hz), 1.09 (12H, d, $J$=6.7 Hz), 1.19 (12H, d, $J$=7.0 Hz), 2.79 (2H, hept, $J$=7.0 Hz), 3.17 (4H, hept, $J$=6.7 Hz), 7.34 (4H, s); MS (70 eV) *m/z* 615 ($M^+$−Cl), 412, 209; IR 2960, 2870, 1560, 1460, 1420, 1380, 1360, 1100, 875, 740 cm$^{-1}$. Found C, 54.86; H, 7.13%. Calcd for $C_{30}H_{46}BiCl$: C, 55.34; H, 7.12%.

**Methylbis(2,4,6-triisopropylphenyl)bismuthine (4):** To a yellowish solution of **3c** (329 mg, 0.5 mmol) in THF (10 ml) was added methyllithium (1.0 M ether solution; 0.5 ml, 0.5 mmol) at −78 °C. After stirring for 10 min at −78 °C, the reaction mixture was allowed to warm to room temperature and the solvent was evaporated under reduced pressure. Chromatography of a solid residue on silica gel gave **4** as a colorless crystalline solid (262 mg, 77%). Mp 53—55 °C (pentane–ether). $^1$H NMR $\delta$=0.98 (12H, d, $J$=6.7 Hz), 1.03 (12H, d, $J$=6.7 Hz), 1.19 (12H, d, $J$=7.0 Hz), 1.69 (3H, s), 2.80 (2H, hept, $J$=7.0 Hz), 3.00 (4H, hept, $J$=6.7 Hz), 6.98 (4H, s); MS

(70 eV) *m/z* 615, 426, 412, 209; IR 2960, 1555, 1460, 1415, 1380, 1360, 1095, 1000, 875, 740 cm$^{-1}$. Found: C, 59.56; H, 7.99%. Calcd for $C_{31}H_{49}Bi$: C, 59.04; H, 7.83%.

**(2-Phenylethenyl)bis(2,4,6-triisopropylphenyl)bismuthine (5):** To a THF (10 ml) solution of 2-phenylethenyllithium prepared from *n*-BuLi (1.4 M hexane solution, 0.8 ml, 1.1 mmol) and (2-phenylethenyl)tributylstannane (431 mg, 1.1 mmol) was added a THF solution (10 ml) of **3c** (650 mg, 1 mmol) at −78 °C under an argon atmosphere. The resulting mixture was stirred for 1 h at room temperature and then poured into ice-water. The aqueous layer was extracted with ether (10 ml×2) and the combined extracts were washed with brine (10 ml×2). Evaporation of the solvent left a pale yellow oil, which was recrystallized from pentane/ether to give **5** as a pale yellow crystalline solid (445 mg, 62%). Mp 139—141 °C. $^1$H NMR $\delta$=0.99 (12H, d, $J$=6.8 Hz), 1.04 (12H, d, $J$=6.8 Hz), 1.19 (12H, d, $J$=6.9 Hz), 2.80 (2H, hept, $J$=6.9 Hz), 3.12 (4H, hept, $J$=6.9 Hz), 7.04 (4H, s), 7.2—7.4 (5H, m), 7.45 (1H, d, $J$=17.9 Hz), 9.59 (1H, d, $J$=17.9 Hz); MS (70 eV) *m/z* 615, 515, 412, 291, 209, 204, 189, 161, 133, 119, 109; IR 2900, 1458, 1416, 1383, 1362, 1051, 970 cm$^{-1}$. Found: C, 63.21; H, 7.49%. Calcd for $C_{38}H_{53}Bi$: C, 63.50; H, 7.43%.

**(2-Arylethynyl)bis(2,4,6-triisopropylphenyl)bismuthines (6a—c):** To a THF (10 ml) solution of lithium acetylide prepared from *n*-BuLi (1.4 M hexane solution, 1.2 ml, 1.7 mmol) and an appropriate arylacetylene (1.4 mmol) was added a THF (10 ml) solution of **3c** (910 mg, 1.4 mmol) at −78 °C under argon. The resulting mixture was stirred for 1 h at room temperature and then poured into ice-water. The aqueous layer was extracted with ether (10 ml×2) and the combined extracts were washed with brine (10 ml×2). Evaporation of the solvent gave a yellow powder, which was recrystallized from pentane/ether to give **6** as a pale yellow crystalline solid.

**(2-Phenylethynyl)bis(2,4,6-triisopropylphenyl)bismuthine (6a).** Mp 139—141 °C (pentane-ether). $^1$H NMR $\delta$=1.06 (12H, d, $J$=6.6 Hz), 1.07 (12H, d, $J$=6.6 Hz), 1.20 (12H, d, $J$=7.0 Hz), 2.81 (2H, hept, $J$=7.0 Hz), 3.28 (4H, hept, $J$=6.6 Hz), 7.11 (4H, s), 7.22—7.41 (5H, m); MS (70 eV) *m/z* 615, 512, 412, 410, 209; IR 2960, 1490, 1460, 1380, 1360, 880, 750, 690 cm$^{-1}$. Found: C, 63.69; H, 7.42%. Calcd for $C_{38}H_{51}Bi$: C, 63.67; H, 7.17%.

**[2-(4-Methylphenyl)ethynyl]bis(2,4,6-triisopropylphenyl)bismuthine (6b).** Mp 127—129 °C (pentane-ether). $^1$H NMR $\delta$=1.05 (12H, d, $J$=6.6 Hz), 1.06 (12H, d $J$=6.6 Hz), 1.19 (12H, d, $J$=7.0 Hz), 2.33 (3H, s), 2.80 (2H, hept, $J$=7.0 Hz), 3.28 (4H, hept, $J$=6.7 Hz), 7.07 (2H, d, $J$=8.1 Hz), 7.11 (4H, s), 7.30 (2H, d, $J$=8.1 Hz); MS (70 eV) *m/z* 615, 573, 412, 410, 275, 209; IR 2960, 1560, 1510, 1460, 1420, 1380, 1360, 880, 820, 720 cm$^{-1}$. Found: C, 63.98; H, 7.41%. Calcd for $C_{39}H_{53}Bi$: C, 64.10; H, 7.31%.

**[2-(4-Chlorophenyl)ethynyl]bis(2,4,6-triisopropylphenyl)bismuthine (6c).** Mp 105—107 °C (pentane-ether). $^1$H NMR $\delta$=1.05 (12H, d, $J$=6.6 Hz), 1.06 (12H, d, $J$=6.7 Hz), 1.20 (12H, d, $J$=6.9 Hz), 2.81 (2H, hept, $J$=6.7 Hz), 3.25 (4H, hept, $J$=6.7 Hz), 7.12 (4H, s), 7.23 (2H, d, $J$=8.7 Hz), 7.32 (2H, d, $J$=8.5 Hz) MS (70 eV) *m/z* 615, 573, 447, 412, 410, 209; IR 2970, 1560, 1480, 1460, 1200, 1090, 870, 830 cm$^{-1}$. Found: C, 61.16; H, 6.94%. Calcd for $C_{38}H_{50}BiCl$: C, 60.75; H, 6.71%.

**Iododimesitylbismuthine (7):** According to the reported procedure for the synthesis of iododiphenylbismuthine,[11] **7** was prepared by the reaction of chlorodimesitylbismuthine with sodium iodide; the chlorobismuthine was obtained by the metathesis reaction between **2a** and $BiCl_3$. Orange colored crystals (pentane-ether). Mp 135—137 °C (decomp). $^1$H NMR $\delta$=2.26 (6H, s), 2.39 (12H, s), 7.17 (4H, s); MS (70 eV) *m/z* 447, 327, 237, 209, 167, 119; IR 2910, 1590, 1440, 1375, 1290, 1030, 995, 855 cm$^{-1}$. Found: C, 38.29; H, 4.07%. Calcd for $C_{18}H_{22}BiI$: C, 37.65; H, 3.86%.

**Dimesitylmethylbismuthine (8):** According to a procedure similar to that used for the preparation of **4**, bismuthine **8** was obtained in 84% yield by the reaction of **7** with methyllithium. Pale yellow crystals (pentane). Mp 44—45 °C (lit, 51 °C).[6] $^1$H NMR 1.60 (3H, s), 2.24 (6H, s), 2.27 (12H, s), 6.90 (4H, s); MS (70 eV) *m/z* 447, 342, 327, 209, 119, 91, 77; IR 2920, 1450, 1290, 850, 700 cm$^{-1}$. Found: C, 49.76; H, 5.52%. Calcd for C, 49.35; H, 5.45%.

**Dimesityl(2-phenylethynyl)bismuthine (9):** According to a similar procedure described above, bismuthine **9** was obtained in 84% yield by the reaction of **7** with lithium phenylethynylide. Pale yellow crystals (pentane-ether). Mp 112—114 °C. $^1$H NMR $\delta$=2.24 (6H, s), 2.43 (12H, s), 7.01 (4H, s), 7.2—7.4 (5H, m); MS (70 eV) *m/z* 447, 328, 237, 220, 209, 202, 189, 165, 119, 115, 101; IR 3013, 1595, 1445, 1288, 1208, 1024, 849, 787, 756 cm$^{-1}$. Found: C, 53.90 H, 4.89%. Calcd for $C_{26}H_{27}Bi$: C, 56.94; H, 4.96%.

**Reaction of 4 with Sulfuryl Chloride:** To a dichloromethane (10 ml) solution of bismuthine **4** (315 mg, 0.5 mmol) was added sulfuryl chloride (0.5 mmol) at −40 °C under an argon atmosphere. As the solution was warmed gradually up to room temperature, the color of the reaction mixture turned yellow. After 1 h the solvent was removed under reduced pressure to leave an oil, which was chloride **3c** (95%) accompanied by a slight amount of 1,3,5-triisopropylbenzene.

**Reaction of 6b with Benzoyl Chloride:** To a benzene (5 ml) solution of bismuthine **6b** (210 mg, 0.29 mmol) was added benzoyl chloride (0.9 mmol) at room temperature. After heating at 80 °C for 4 h, the reaction mixture was poured into ice-water. The aqueous layer was extracted with ether (5 ml×2) and the combined extracts were worked up as usual. The residue was chromatographed over a silica-gel column using hexane/benzene as an eluent to give **10** (34 mg, 51%) and **3c** (114 mg, 65%).

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3) When dissolved in chloroform and left to stand in open air, bismuthine **2b** suffered a slow decomposition to yield 1,3,5-triethylbenzene and an insoluble polymeric substance.

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