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SYNTHESIS AND HALOGENOLYSIS OF STABLE PENTACOORDINATE BISMUTH COMPOUNDS (10-Bi-5): FORMATION OF 1-CHLORO-1,1-DIARYL-3,3-BIS(TRIFLUOROMETHYL)-3H-2,1-BENZOXABISMOLES

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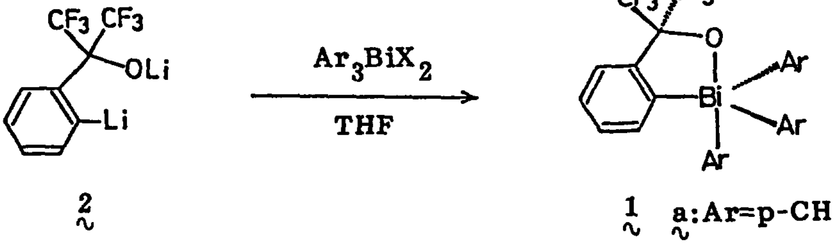
Abstract: A stable pentacoordinate bismuth compound (1) with a five-membered ring was synthesized. Reaction of 1 with sulfuryl chloride afforded a novel stable compound (4) with a covalent Bi-Cl bond. The compound was useful for the synthesis of other hypervalent bismuth compounds with different Bi-C bonds such as 1c, and the selectivity in the chlorination of 1c was described.

The bismuth-carbon bond is one of the weakest bonds among the typical element-carbon bonds; the bond energy of $BiMe_3$ (146 kJ/mol) is even smaller than that of $PbMe_4$ (168 kJ/mol).[1] The hypervalent compounds of such typical elements should contain weaker and more polarizable bonds than ordinary ones, hence unique reactivity is expected. In fact, Barton et al. reported interesting works on the phenylation of phenols, amines, and etc. using well-designed pentacoordinate bismuth compounds.[2] The weakness of the bismuth-carbon bond, however, has been preventing the synthesis of elementary hypervalent bismuth compounds, the number of isolated ones is still relatively few.[3] Now we report the preparation of a stable 10-Bi-5[4] compound (1) by use of a five-membered ligand (2)[5] and the halogenolysis of 1 to form a novel stable 1-chloro derivative (4).

1,1,1-Triaryl-3,3-bis(trifluoromethyl)-3H-2,1-benzoxabismole(V) (1) was prepared in 61 % and 53 % yield by the reaction of Ar_3BiBr_2 or Ar_3BiCl_2 and the dilithiated reagent (2) of bis(trifluoromethyl)benzyl alcohol.[6] Compound 1 could be purified on TLC (SiO_2) to give colorless crystals (mp, a: 207-209; b: 199-201 °C) and gave correct elemental analyses.[7] It is quite stable in comparison with other reported Bi(V) compounds containg Bi-C bonds, which are usually sensitive to heat and atmospheric moisture.[3]

Scheme 1

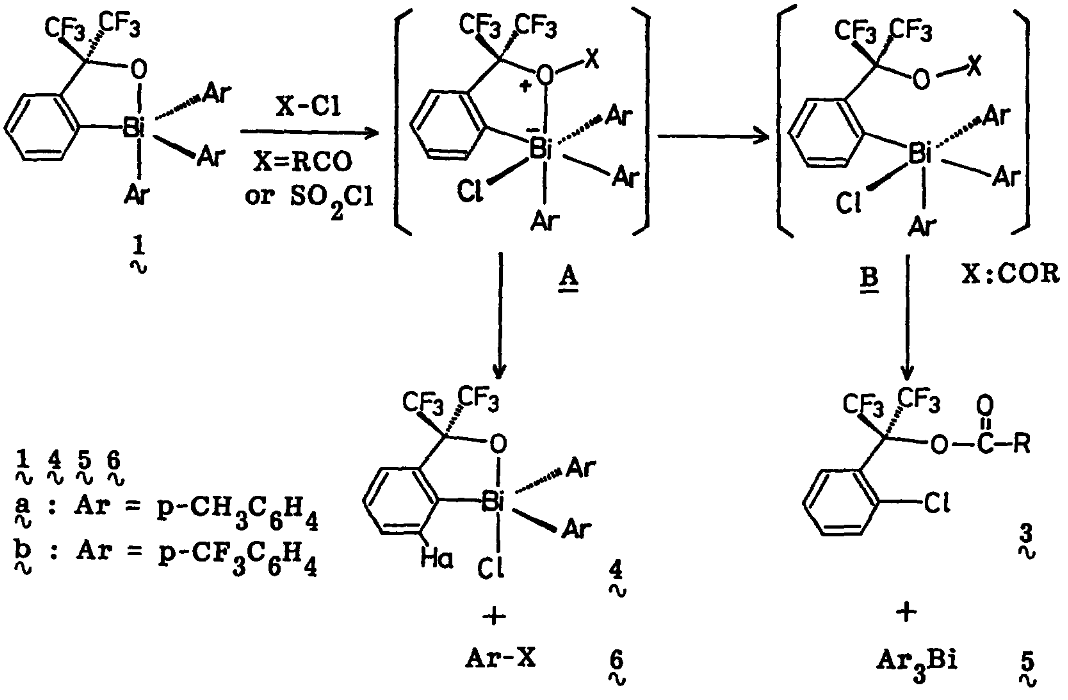


2

1 a:Ar=p-$CH_3C_6H_4$
b:Ar=p-$CF_3C_6H_4$

1 was more reactive to electrophilic reagents, however, than the corresponding antimony compound which was inert to almost all the electrophilic reagents.[8] Thus ethyl succinyl chloride reacted with **1a** in benzene at 50 °C for 8.5 h to give **3**, **4a**, and **5a** in 84 %, 8 %, and 61 % yield, respectively.[9,10] In contrast, the reaction of sulfuryl chloride with **1** in CH_2Cl_2 afforded **4** and **6** almost quantitatively (>95 %) at room temperature. No other product was detected in the reaction. **4** could be recrystallized from benzene-ethanol to form colorless crystals (mp, **a**: 186-189; **b**: 106<(dec) °C) and gave correct elemental analyses. The structure of **4** is interesting in relation to the recent concern for the (covalent or ionic) nature of the hypervalent element-halogen bond.[11] In the ^1H NMR ($CDCl_3$) of **4**, the aromatic ortho proton (H_a) appeared at rather low field (**a**: δ 8.74, dd, J=7.5, 1.4 Hz; **b**: δ 8.69, dd, J=7.6, 1.2 Hz), indicating the presenc of the polarizable hypervalent Bi-Cl bond.[11a] The high solubility of **4** in nonpolar solvents such as benzene and chloroform and also stability to ethanol are supporting that the nature of the Bi-Cl bond is covalent. The most stable structural isomer of **4** is considered to be the trigonal bipyramidal one with the chlorine atom at the apical position as shown in scheme 2, since the more electronegative groups are well known to prefer the apical positions (apicophilicity).[12]

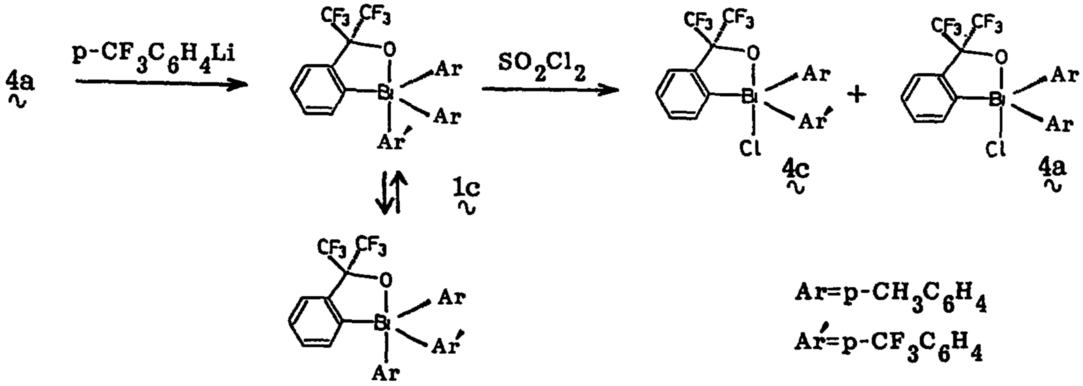
Scheme 2



1 **4** **5** **6**
a : Ar = $p\text{-}CH_3C_6H_4$
b : Ar = $p\text{-}CF_3C_6H_4$

4 is a very useful precursor in order to prepare other hypervalent species, for example, p-trifluoromethylphenyl lithium reacted with **4a** to give **1c** in 63 % yield.[13] **1c** also gave correct elemental analyses, and is an interesting compound with different kinds of Bi-C bonds, i.e., Bi-tolyl and Bi-trifluoromethylphenyl. Although such well-defined unsymmetrical hypervalent compounds are quite few due to the difficulty in preparation, these must be useful for the investigation on the reactivity of the hypervalent bonds such as ligand-ligand coupling from Sb(V) species.[14] In fact, the chlorination of **1c** with sulfuryl chloride was carried out to shed light on the mechanism of halogenolysis. The reaction took place smoothly to give **4c**[15] and **4a** (>10:1) in almost quantitative yield. Thus the electron-rich Bi-tolyl bond reacted selectively. A simple possible explanation of the result was illustrated in scheme 2, thus the electrophiles reacted at the oxygen atom of **1** to form an intermediate A and A collapsed to give **4** by syn-elimination of **6** and to **3** and **5** via B. Alternatively, the initial reaction site of the reagents may be different, namely sulfuryl chloride may attack directly the Bi-carbon bond. Further investigation on the mechanism of these transformations is now in progress.

Scheme 3



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4. N-X-L designation: X, central atom; N, formal valence shell electrons about an X; L, the number of ligands. (see C. W. Perkins, J. C. Martin, A. J. Arduengo, W. Lau, A. Algeria, and J. K. Kochi, J. Am. Chem. Soc., 102, 7753 (1980).)
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6. Preparation of **1a**: The dilithiated reagent (**2**) was prepared by the method reported previously[4] (BuLi 72.1 mmol, N,N,N',N'-tetramethylethylenediamine 7.3 mmol, hexafluorocumyl alcohol 32.9 mmol, THF 5 ml). To a diluted stirred solution of **2** in 50 ml of THF a solution of $(p\text{-}CH_3C_6H_4)_3BiBr_2$ (23.4 mmol) in 100 ml of THF was added dropwise at -78 °C. The mixture was stirred for 24 h at room temperature, and was quenched with aqueous sodium chloride. The product was extracted with ether. The combined solution was evaporated and the residue was subjected to short column chromatography (SiO_2, hexane, and then hexane-ethyl acetate (12:1)) to afford crude **1**, which was recrystallized from ether-hexane.
7. **1a**: ^1H NMR ($CDCl_3$) δ 2.37 (s, 9H), 7.28 (d, 6H, J=8Hz), 7.64 (d, 6H, J=8Hz), 7.37-7.55 (m, 3H), 7.91-8.13 (m, 1H). ^{19}F NMR ($CDCl_3$) δ -73.4 (s, 6F). Anal. Calcd. for $C_{30}H_{25}BiF_6O$: C, 49.73; H, 3.48. Found: C, 49.80; H, 3.46.
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9. **3**: ^1H NMR ($CDCl_3$) δ 1.24 (t, 3H, J=7Hz), 2.50-3.10 (m, 4H), 4.15 (q, 2H, J=7Hz), 7.2-7.7 (m, 4H).
10. **4a**: ^1H NMR ($CDCl_3$) δ 2.38 (s, 6H), 7.43 (d, 4H, J=8Hz), 7.60-8.05 (m, 3H), 8.17 (d, 4H, J=8Hz), 8.73 (d, 1H, J=7Hz). ^{19}F NMR ($CDCl_3$) δ -74.1 (s, 6F). Anal. Calcd for $C_{23}H_{18}BiClF_6O$: C, 41.30; H, 2.71. Found: 41.07; H, 2.70.
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13. **1c**: mp 182-185 °C (ether-hexane). ^1H NMR ($CDCl_3$) δ 2.39 (s, 6H), 7.1-8.2 (m, 16H). ^{19}F NMR (acetone-d_6) δ -74.9 (s, 6F), -63.4 (s, 3F). Anal. Calcd for $C_{30}H_{22}BiF_9O$: C, 46.29; H, 2.85. Found: C, 46.39; H, 2.75.
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15. **4c**: mp 141-142 °C. ^1H NMR ($CDCl_3$) δ 2.38 (s, 3H), 7.46 (d, 2H, J=8.4Hz), 7.5-8.0 (m, 5H), 8.19 (d, 2H, J=8.4Hz), 8.50 (d, 2H, J=8.6Hz), 8.71 (dd, 1H, J=7.6, 1.4Hz). ^{19}F NMR ($CDCl_3$) δ -74.4 (s, 6F), -62.9 (s, 3F). Anal. Calcd for $C_{23}H_{15}BiClF_9O$: C, 38.22; H, 2.09. Found: C, 38.51; H, 2.12.

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