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Preparation and Properties of Alkyl Diarylbismuthinates. A New Class of Organic Pentavalent Bismuth Compounds

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Methyl diarylbismuthinates, a new class of organic pentavalent bismuth compounds, were prepared by the reaction of triarylbismuthines with chloramine-T in methanol and their chemical properties were investigated. These compounds possess a mild and selective oxidizing ability.

Recently increasing attention has been paid to the organic field of bismuth chemistry.1) Compared with other group 5B elements, the number of known organic bismuth compounds are as yet limited. Even the ylides of bismuth were well characterized only recently.2) Bismuthinates (R_2BiOOR'), pentavalent bismuth esters which are analogues of phosphinates (R_2POOR'), represent one of structurally basic bismuth compounds; however, they are unknown to date as far as we are aware. Herein we wish to report a simple preparative method for them for the first time and disclose some of their chemical properties.

Methyl diarylbismuthinates (**4**) were prepared by the reaction of triarylbismuthines (**1**) with N-chloro-4-methylphenylsulfonamide sodium salt hydrate (chloramine-T hydrate) in methanol. Typically, tris(4-methyl-1-naphthyl)bismuthine (**1h**) (632 mg, 1 mmol) and chloramine-T (564 mg, 2 mmol) were heated in benzene (20 ml)/ methanol (20 ml) for ca. 30 min. When the triarylbismuthine was consumed completely, the precipitated solid was filtered off, the solution was concentrated in vacuo to ca. 20 ml, and left to stand. Crystalline deposit obtained were filtered, washed with methanol, and recrystallized from benzene/methanol to give pale yellow fine needles (446 mg), which were assigned as methyl bis(4-methyl-1-naphthyl)bismuthinates (**4h**) from elemental and spectral data.3) 1-Methylnaphthalene (123 mg, 0.87 mmol) and 4-methylphenylsulfonamide (205 mg, 1.20 mmol) were by-

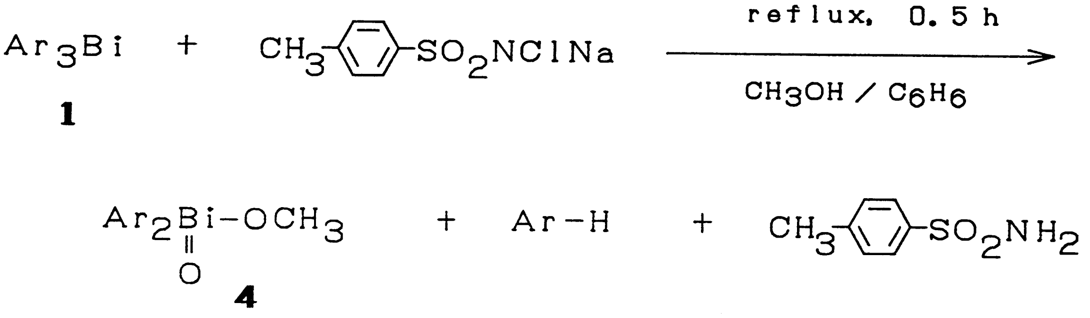


Table 1. Preparation of methyl diarylbismuthinates (**4**) from triarylbismuthines (**1**)

	Aryl	Yield /%
a.	phenyl	30
b.	4-methylphenyl	10
c.	2-methylphenyl	60[a)]
d.	3,4-dimethylphenyl	20
e.	3-trifluoromethylphenyl	0[b)]
f.	4-chlorophenyl	0[b)]
g.	1-naphthyl	80
h.	4-methyl-1-naphthyl	80
i.	2-thienyl	0[c)]

a) Bis(2-methylphenyl)bismuthinic acid was obtained.

b) Triarylbismuthine was consumed completely; however, disproportionation occurred during the work-up to regenerate triarylbismuthine.

c) Insoluble colorless solid was obtained.

Table 2. Ester exchange of diarylbismuthinates

$$Ph_2BiOOR^1 \xrightarrow[R^2OH]{} Ph_2BiOOR^2$$

R^1	R^2	Yield/%
Me	Et	60
Et	Me	83
Me	i-Pr	52
Me	H	90

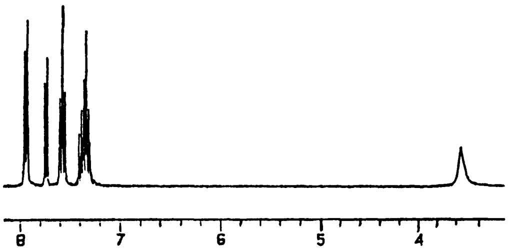


Fig. 1. ^{1}H-NMR of methyl diphenylbismuthinate. A broad signal at δ =3.58 is due to the methoxy protons.

products.

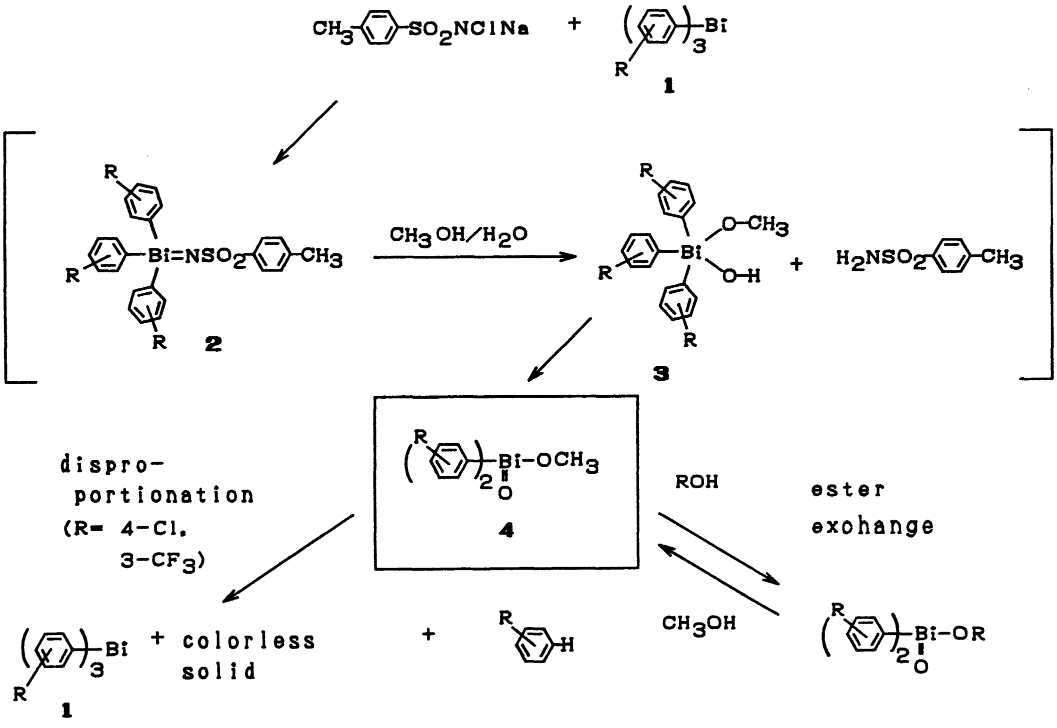
Other examples are shown in Table 1 and spectral data of several bismuthinates and related compound are presented in Ref. 3. Triphenylbismuthine (**1a**), tris(2-methylphenyl)bismuthine (**1c**), tris(3,4-dimethylphenyl)bismuthine (**1d**), tris(1-naphthyl)bismuthine (**1g**), and tris(4-methyl-1-naphthyl)bismuthine (**1h**) all afforded the corresponding bismuthinates in moderate to good yields. Tris(4-methylphenyl)bismuthine (**1b**) gave the bismuthinate **4b** in a low yield; it underwent a facile disproportionation during purification to give the starting triarylbismuthine **1b**. None of bismuthinates were obtained from the reactions of tris(4-chlorophenyl)bismuthine (**1f**) and tris(3-trifluoromethylphenyl)bismuthine (**1e**). Judging from thin layer chromatography of the initial product mixture, these triarylbismuthines were consumed completely; after working-up, however, no bismuthinates were obtained and triarylbismuthines **1e** and **1f** were recovered in ca. 60% yields. The disproportionation of bismuthinates (**4**) to bismuthines (**1**) was not observed with **4c**, **4g**, and **4h**. Probably, steric crowdedness around the bismuth atom prevented the bismuthinates from undergoing disproportionation.

^{1}H-NMR signals for methoxy groups of these bismuthinates appear as unusually broad single peak at δ 3.5-3.6 as is illustrated in Fig 1. This might indicate that the methoxy group moves around several sites of different magnetic environments within the molecule, which is probably caused by lability of the Bi-

OCH_3 bond. The weakness of Bi-OCH_3 bond was further evidenced by a facile ester exchange of the bismuthinates. When methyl diphenylbismuthinate was recrystallized from ethanol, ethyl diphenylbismuthinate was obtained as the sole product in 60% yield. Other examples of the ester exchange are tabulated in Table 2.

Next, we examined an oxidizing ability of the bismuthinates. When a mixture of methyl bis(1-naphthyl)bismuthinate (260 mg, 0.51 mmol) and benzoin (216 mg, 1.02 mmol) was heated in benzene (10 ml) under reflux for 2h, benzil (170 mg, 0.81 mmol), unchanged benzoin (30 mg, 0.14 mmol), naphthalene (116 mg, 0.91 mmol), and metallic bismuth (105 mg) were obtained. Heating the bismuthinate with 1,1,2,2-tetraphenyl-1,2-ethanediol in benzene under reflux for 10 - 30 min led to benzophenone quantitatively. Hydrazobenzene afforded azobenzene quantitatively, and 1,2-diphenyl-1,2-ethanedione dihydrazone gave diphenylacetylene in a 50% yield. However, non-activated glycols such as 1,2-cyclohexanediol and 1-phenyl-1,2-ethanediol were recovered unchanged. Sodium bismuthate ($NaBiO_3$) is known to perform the glycol fission efficiently. Compared with this classical reagent, the bismuthinates appear to possess a milder and more selective oxidizing ability.

As for the formation of bismuthinates we propose a possible reaction mechanism shown in Scheme 1. Bismuthonium imine 2 formed from triarylbismuthine 1 and chloramine-T$^{4)}$ undergoes solvolysis with alcohol and water adventitiously present in the solvent to form the intermediate (3), which collapses into bismuthinate 4 and aromatic hydrocarbon. Analogous imines of other group 5B elements (P, As) are known to be stable toward alcohols,$^{5)}$ and this type of transformations has not been reported previously. Thus, the highly reactive bismuthonium imines may be expected as a good precursor for a variety of pentavalent bismuth compounds.



Scheme 1. A possible scheme for the formation of bismuthinates

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3) **Methyl diphenylbismuthinate**; mp 110-120 °C (dec); IR (KBr) 3050, 1570, 1475, 1430, 1020, 725 and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.58 (bs, 3H) and 7.1-8.2 (m, 10H). Found: C, 37.87; H, 2.99%. Calcd for $C_{13}H_{13}BiO_2$: C, 37.81; H, 3.17%.

Methyl bis(3,4-dimethylphenyl)bismuthinate; mp 90-100 °C (dec); IR (KBr) 2930, 1590, 1495, 1455, 1395, 1015, 820, 775 and 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.13 (s, 12H), 3.60 (bs, 3H) and 7.1-8.2 (m, 6H). Found: C, 43.69; H, 4.49%. Calcd for $C_{17}H_{21}BiO_2$: C, 43.79; H, 4.53%.

Methyl bis(1-naphthyl)bismuthinate; mp 135-145 °C (dec); IR (KBr) 3040, 1620, 1580, 1555, 1500, 1455, 1390, 1335, 1260, 1215, 1140, 1030, 795 and 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.48 (bs, 3H) and 7.0-8.8 (m, 14H). Found: C, 50.25; H, 3.23%. Calcd for $C_{21}H_{17}BiO_2$: C, 49.42; H, 3.36%.

Methyl bis(4-methyl-1-naphthyl)bismuthinate; mp 140-150 °C (dec); IR (KBr) 3050, 2905, 1590, 1505, 1450, 1390, 1365, 1210, 1035, 830 and 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.60 (s, 6H), 3.50 (bs, 3H) and 7.0-8.6 (m, 12H); Found: C, 51.54; H, 4.05%. Calcd for $C_{23}H_{21}BiO_2$: C, 51.31; H, 3.93%.

Ethyl diphenylbismuthinate from methyl diphenylbismuthinate; mp 140-150 °C (dec); IR (KBr) 3040, 1570, 1475, 1430, 1025, 725 and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.23 (t, J=7.0 Hz, 3H), 3.76 (bm, 2H), 7.3-8.0 (m, 10H). Found: C, 39.93; H, 3.69%. Calcd for $C_{14}H_{15}BiO_2$: C, 39.64; H, 3.56%.

Bis(2-methylphenyl)bismuthinic acid; mp 110-130 °C (dec); IR (KBr) 3050, 3000-2900, 1580, 1450, 1380, 1275, 1205, 1165, 1125, 1040, 845, and 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.23 (bs, 6H), 7.0-8.2 (m, 8H). Found: C, 40.01; H, 3.71%. Calcd for $C_{14}H_{15}BiO_2$: C, 39.64; H, 3.56%.

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