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A Novel Synthesis of Alkylbismuthonium Salts and their Reaction with Some Nucleophiles. First X-Ray Structural Analysis of a Stabilized Alkylbismuthonium Tetrafluoroborate

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Abstract: Treatment of triarylbismuth difluorides **1** with silyl enol ethers **2** in the presence of BF_3•OEt_2 gives (2-oxoalkyl)triarylbismuthonium tetrafluoroborates **3** as a stable crystalline solid, the bismuth centre of which has been found by X-ray analysis to possess a tetragonal geometry. The 2-oxoalkyl moiety of compound **3** couples with enolates and thiolates to afford the corresponding triketones **4** and α-thioketones **6**, respectively.

In marked contrast to lighter pnictogen isologues which involve the bond-forming electrons in an sp^3-hybridized state, bismuthine lays its lone pair of electrons in an *s*-orbital. Because of this unique difference in electronic configuration, organylbismuthines are poor as both a base and a nucleophile, making the bismuthonium salts unavailable through the direct interaction of alkylating agents with organylbismuthines.[1] Literature to date contains only one paper on the isolation of alkylbismuthonium compounds, in which acetonyltriphenylbismuthonium perchlorate and tetrafluoroborate were obtained from the metathetical reaction of triphenylbismuth dichloride with corresponding silver(I) salts in dry acetone.[2] This approach, however, appears to lack generality as a preparative method for the bismuthonium salts because compatible organyl ligands were quite limited. We report herein a novel efficient synthesis of (2-oxoalkyl)triarylbismuthonium salts and their reaction with some nucleophiles. The first X-ray structure analysis of a stabilized alkylbismuthonium salt, (3,3-dimethyl-2-oxobutyl)triphenylbismuthonium tetrafluoroborate **3a**, revealed the tetragonal geometry of the bismuth centre in support of the onium character of compound **3**.

Since the bismuthines are too weak a nucleophile to react with alkyl halides, we chose a combination of electrophilic bismuth(V) compound and electron-rich ligand-transfer reagent to construct an alkylbismuthonium structure. Thus, treatment of triarylbismuth difluorides **1** with silyl enol ethers **2** in the presence of boron trifluoride etherate successfully led to the corresponding (2-oxoalkyl)triarylbismuthonium tetrafluoroborates **3** in high yields (Scheme 1). A representative procedure is as follows: To a dichloromethane (5 ml) solution of triphenylbismuth difluoride **1a** (478 mg, 1 mmol) was added dropwise BF_3•OEt_2 (0.12 ml, 1 mmol) at 0 °C under argon. After stirring for 1 h, 3,3-dimethyl-2-(trimethylsiloxy)-1-butene **2a** (172 mg, 1 mmol) was introduced and the resulting mixture was stirred for additional 10 h at room temperature to complete the reaction. Evaporarion of the solvent under reduced pressure left an oily residue, which was recrystalized from ether-dichloromethane (2:1) to give bismuthonium salt **3a** (601 mg, 96 %) as colorless crystals. In the absence of $BF_3 \cdot OEt_2$, no reaction took place between **1a** and **2a**. Similarly, the present method was applied to the synthesis of several other bismuthonium salts (Table 1). All isolated compounds are thermally stable and can be handled without change in open air. They are readily soluble in common polar solvents such as dichloromethane, chloroform and acetonitrile without decomposition. Since quaternary bismuth halides readily decompose at room temperature,[3] low nucleophilicity of the tetrafluoroborate anion should be an essential factor to stabilize compounds **3**. The present method is superior to the reported ones[2-4] in that the procedure is simpler and generally applicable.

Scheme 1

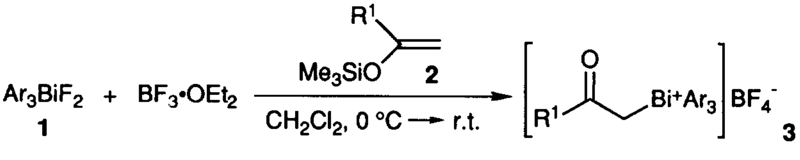

Table 1 (2-Oxoalkyl)triarylbismuthonium salts (3) obtained

Entry	Ar (**1**)	R^1 (**2**)	Compound (**3**)	Yield/%[a]	M.p./°C
1	Ph (**1a**)	*tert*-C_4H_9 (**2a**)	**3a**	96	143-145
2	Ph (**1a**)	*sec*-C_4H_9 (**2b**)	**3b**	95	118-119
3	Ph (**1a**)	*iso*-C_3H_7 (**2c**)	**3c**	99	156-157
4	Ph (**1a**)	Ph (**2d**)	**3d**	97	165-167
5	Ph (**1a**)	*p*-BrC_6H_4 (**2e**)	**3e**	94	65-67
6	*p*-Tol (**1b**)	*tert*-C_4H_9 (**2a**)	**3f**	93	96-98
7	*p*-Tol (**1b**)	*sec*-C_4H_9 (**2b**)	**3g**	90	142-144
8	*p*-Tol (**1b**)	Ph (**2d**)	**3h**	87	142-144

[a] Isolated yields. All new products gave satisfactory spectral and analytical data.

An X-ray diffraction study of compound **3a** revealed a crystal structure consisting of discrete bismuthonium and tetrafluoroborate ions as shown in Figure 1.[5] The coordination geometry around the bismuth atom can be described as a distorted tetragon with the bond angles C-Bi-C = 102.1(7)-118.4(7)°, which clearly endorse the onium nature of the bismuth center. Especially, the C_{13}-Bi-C_{19} angle open to the carbonyl oxygen side is appreciably larger (118.4(7)°) than the expected value (109°28'), while the C_1-Bi-C_7 angle is a bit smaller (102.1(7)°). Another noteworthy feature of this molecule is the distance between the bismuth and carbonyl oxygen atoms 2.90(1) Å, which is longer than the sum of the covalent radii (2.10 Å) but much shorter than that of the estimated van der Waals radii (3.72 Å).[7] These findings are suggestive of the operation of an intramolecular interaction between the carbonyl oxygen and electron-deficient bismuth atoms. To date only two papers dealing with crystallographic studies of tetraarylbismuthonium compounds have appeared.[8,9] Our result provides the first example of the structural characterization of alkylbismuthonium compound, which has so far not been accessible by the direct interaction between organylbismuthine and simple halogenoalkanes.

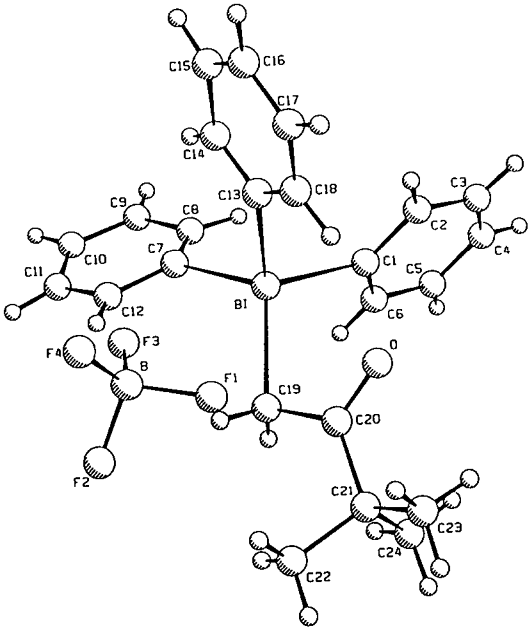

Figure 1. A PLUTO drawing of compound **3a** with the atomic numbering scheme. Selected interatomic distances (Å) and angles (°) : Bi-C(1) 2.20(2), Bi-C(7) 2.21(2), Bi-C(13) 2.19(2), Bi-C(19) 2.20(2), C(19)-C(20) 1.49(2), C(20)-O 1.22(2), Bi••O 2.90(1), Bi••F(3) 3.48(1); C(1)-Bi-C(7) 102.1(7), C(1)-Bi-C(13) 107.0(7), C(1)-Bi-C(19) 110.6(6), C(7)-Bi-C(13) 105.6(8), C(7)-Bi-C(19) 111.8(7), C(13)-Bi-C(19) 118.4(7), Bi-C(19)-C(20) 106(1), O-C(20)-C(19) 119(2).

To get a sight into the chemistry of alkylbismuthonium salts, the reaction with some nucleophiles has been examined. The bismuthonium salt **3** readily reacted with enolates from 1,3-dicarbonyl compounds in THF to give the corresponding triketones **4** in moderate yields (Scheme 2, Table 2).

Scheme 2

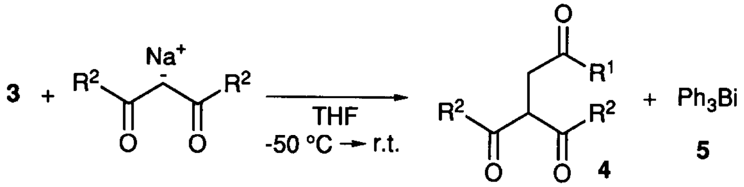

Table 2 Reaction of compound **3** with some enolates

Entry	R^1 (**3**)	R^2	Yield/%^{a}	
1	*iso*-C_3H_7 (**3c**)	Ph	**4a** (69)	**5** (91)
2	*iso*-C_3H_7 (**3c**)	OCH_3	**4b** (56)	**5** (87)
3	*iso*-C_3H_7 (**3c**)	OC_2H_5	**4c** (70)	**5** (92)
4	Ph (**3d**)	Ph	**4d** (61)	**5** (92)
5	*p*-BrC_6H_4 (**3e**)	Ph	**4e** (60)	**5** (84)

^{a} Isolated yields.

When treated with arylthiolates, the compound **3a** smoothly underwent the C(alkyl)-S coupling to afford α-thioketones **6** in good yields (Scheme 3, Table 3). In both types of reactions, triphenylbismuthine **5** was mostly recovered after column chromatography.

Scheme 3

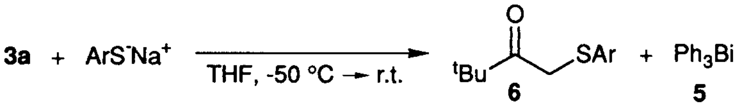

Table 3 Reaction of compound **3a** with some thiolates

Entry	Ar	Yield/%[a]	
1	Ph	**6a** (77)	**5** (84)
2	*p*-ClC_6H_4	**6b** (72)	**5** (80)

[a] Isolated yields.

This is the first example of a definite alkyl transfer from the bismuthonium compounds, the synthetic potentials of which will be subject to our future study.

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References and Notes

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5. Selected spectral data of **3a**: NMR (200 MHz; $CDCl_3$) δ_H 1.26 (s, 9H), 5.60 (s, 2H), 7.52-7.82 (m, 15H). δ_C 26.9, 45.9, 56.9, 131.8, 131.9, 135.8, 137.9, 212.2 ; IR (KBr) ν_{max}/cm^{-1} 3050-2950, 1674 (C=O), 1475, 1437, 1150-950 (BF_4^-), 727, 695 ; MS (FAB) *m/z* 539 (M^+-BF_4), 363, 286, 209. Anal. Found: C, 46.39; H, 4.36; Calcd. for $C_{24}H_{26}BBiF_4O$: C, 46.03; H, 4.18 %. Crystallographic data of compound **3a**.- A crystal of dimensions 0.180 x 0.180 x 0.300 mm, grown from Et_2O-CH_2Cl_2 (2:1), was used. Formula; $C_{24}H_{26}BiOBF_4$, M=626.25. Rhombohedral (hexagonal axes), Space group, R3(h) (#148), a = 30.606(7), c = 14.195(5) Å, V = 11514(6) Å^3, Z = 18, D_c = 1.625 g cm^{-3}. Prisms, μ(MoKα, λ=0.71069 Å) = 69.09 cm^{-1}, F(000) = 5436. Intensity data were recorded on a Rigaku AFC5R diffractometer using graphite-monochromated Mo-Kα radiation with the ω-2θ scan technique to a maximum 2θ-value of 55°. Of the 6052 reflections which were collected, 5684 were unique (R_{int}=0.091). The structure was solved by a combination of the Patterson method and the direct methods to R = 0.049, R_w = 0.045 for 1899 reflections [I>3.00σ(I)] and 280 variable parameters.[6] The non-hydrogen atoms were refined anisotropically.
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