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N-Tosyltriarylbismuthimines. Synthesis and Reactions with Some Electrophiles

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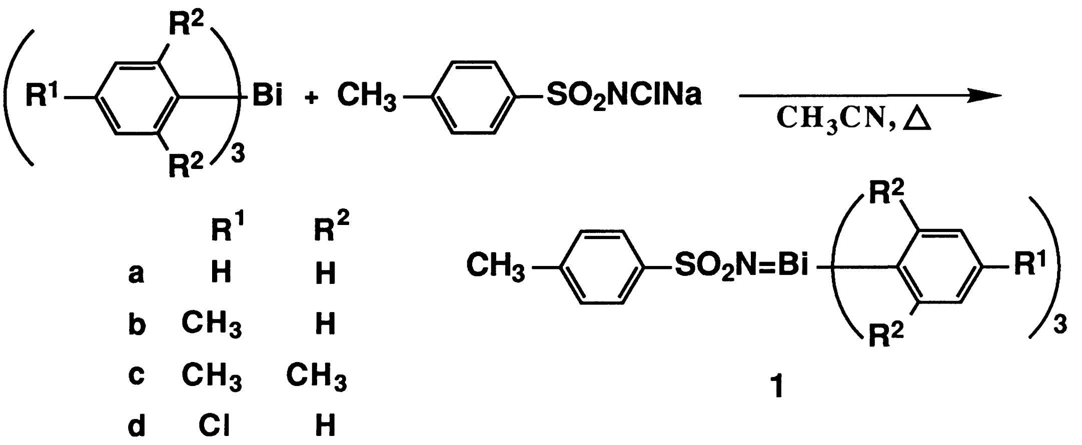
N-Tosyltriarylbismuthimines were prepared by the reaction of triarylbismuthines with chloramine-T and their properties were characterized. These bismuthimines reacted with aromatic aldehydes, acid chlorides, and isocyanates to form N-arylidenetosylamides, N-aroyltosylamides, and N-aryl-N'-tosylureas, respectively. In the presence of copper catalyst, they readily decomposed into N-aryl- and N,N-diaryltosylamides, tosylamide, and triarylbismuthine.

Of all imino compounds derived from stable 15th and 16th Group elements, bismuthimine is the least known and the literature so far contains only one report,1) in which N-tosyltriphenylbismuthimine (**1a**) was obtained as a moisture sensitive solid by the reaction of triphenylbismuthine with chloramine-T in dry acetonitrile under reflux. In the report, little or no properties of this compound were mentioned. In connection with our work on bismuthonium ylides,2-6) we became interested in this type of compounds and tried to prepare **1a** according to the reported procedure.7) In spite of many attempts, however, the isolation of bismuthimine **1a** as a crystalline solid was unsuccessful. The product obtained was either a pale yellow thick oil or a polymeric powder which was nearly insoluble in common organic solvents. Similar treatments of tri-*p*-tolylbismuthine and trimesitylbismuthine with chloramine-T8) gave the corresponding bismuthimines **1b** and **1c** as oily products, which gradually turned into a glassy mass on storage under vacuum. Bismuthimine **1d** from tris(4-chlorophenyl)bismuthine was less stable and gave no satisfactory elemental analysis. Electron-withdrawing substituent on aromatic ring attached to the bismuth atom apparently lowers the stability of bismuthimine **1d**. Some physical properties of four bismuthimines **1a-d** are summarized in Table 1.



	R1	R2
a	H	H
b	CH_3	H
c	CH_3	CH_3
d	Cl	H

1

When methanol was substituted for acetonitrile, methyl diarylbismuthinates were obtained in moderate yields.[9)]

Bismuthimines **1a-c** are moderately stable under dry nitrogen, but readily decompose on standing in open air. They are soluble in acetonitrile, benzene, and dichloromethane; almost insoluble in hexane, and decompose in hydroxylic solvents. In solution bismuthimines were less stable and gradually separated a polymeric substance.

Table 1. Some physical properties of N-tosylbismuthimines (**1**)

Compound		^{1}H NMR δ, ppm vs. TMS [e)]	IR ν / cm^{-1}
1a [a)]	Pale orange oil	2.37(3H,s), 7.2-8.0(19H,m)	1460, 1325, 1155, 1080 920 <NaCl>
1b [b)]	Pale yellow glass	2.30(9H,s), 2.39(3H,s) 7.1-7.9(16H,m)	2920, 1450, 1335, 1160 1090, 920 <KBr>
1c [c)]	Pale yellow glass	1.95(9H,s), 2.00(3H,s), 2.55 (18H,s), 6.64(6H,s), 6.75 (2H,d,*J*=7.9 Hz), 7.68(2H,d, *J*=7.9 Hz)	2920, 1450, 1335, 1160 1070, 940 <KBr>
1d [d)]	Pale yellow oil	2.41(3H,s), 7.1-7.8(16H,m)	1480, 1335, 1160, 1090 925 <NaCl>

a) Found : C, 49.45 ; H, 3.92 ; N, 2.76%. Calcd for $C_{25}H_{22}NO_2SBi$: C, 49.27 ; H, 3.64 ; N, 2.30%.

b) New compound : Found : C, 51.71 ; H, 4.55 ; N, 2.55%. Calcd for $C_{28}H_{28}NO_2SBi$: C, 51.61 ; H, 4.33 ; N, 2.15%. The glassy mass decomposed up to ca. 50 °C without showing any definite melting range.

c) New compound ; no satisfactory analysis was available. The glassy mass decomposed up to ca. 75 °C without showing any definite melting range.

d) New compound ; bismuthimine **1d** was quite unstable and gave no satisfactory analysis.

e) **1a,b,d** : in $CDCl_3$. **1c** : in C_6D_6. Deuterated solvents were dried with molecular sieves 4A before use. Measurements were carried out immediately after the preparation of each sample.

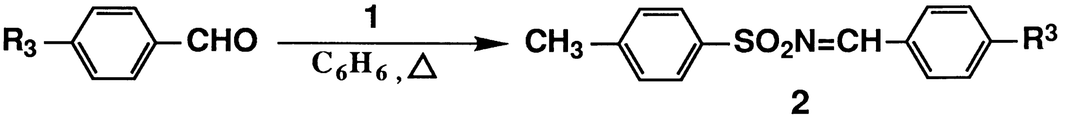
Table 2. N-Arylidenetosylamides (**2**) obtained

R^1	R^2	R^3	Solvent	Yield/%[a)]
H	H	H	CH_3CN	23
H	H	H	C_6H_6	31
H	H	CH_3	C_6H_6	80[b)]
H	H	Cl	C_6H_6	72[b)]
CH_3	H	H	C_6H_6	22
Cl	H	H	C_6H_6	16

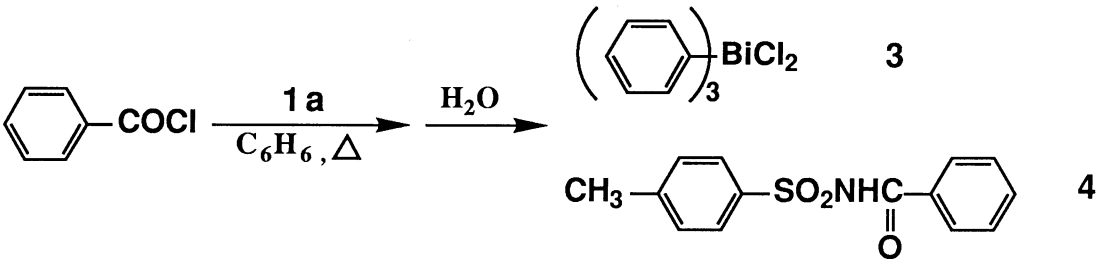
a) Yields refer to the isolated compounds and were not optimized. All products are known. Equimolar bismuthimine and aldehyde were heated for 1 h under reflux.

b) Bismuthimine / aldehyde ratio was 2 to 1.

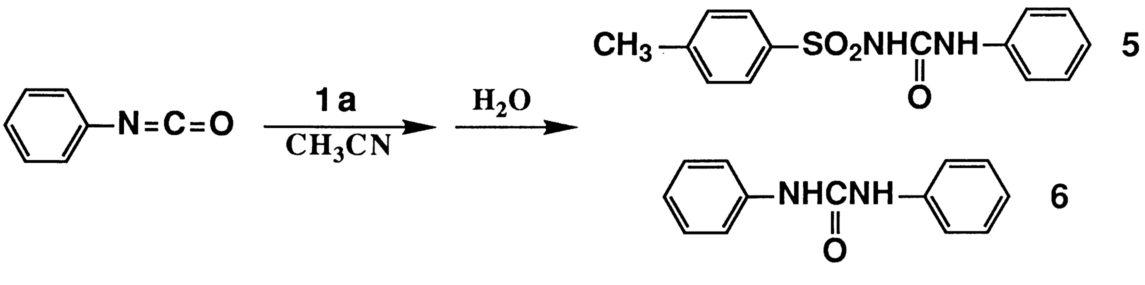
When heated with aromatic aldehydes in benzene under reflux, bismuthimine **1** underwent a reaction analogous to the Wittig reaction, affording N-arylidenetosylamides (**2**) in yields shown in Table 2. Compound **1** failed to react with ketones.



Reaction of bismuthimine **1a** with benzoyl chloride proceeded slowly in hot benzene and gave after 24 h triphenylbismuth dichloride (**3**, 10%) and N-benzoyltosylamide (**4**, 13%) along with a significant amount of bismuth-containing polymeric substance. Benzoyl chloride itself lacks ability to acylate tosylamide under the conditions employed.



Bismuthimine **1a** reacted with phenylisocyanate instantaneously at room temperature and after aqueous work-up N-phenyl-N'-tosylurea (**5**) was obtained in 45% yield along with N,N'-diphenylurea (**6**, 38%). Carbon disulfide was unreactive toward **1**. Anticipating in vain a possible generation of a nitrenoid species, bismuthimine **1** was decomposed under various conditions in the presence of unsaturated compounds. However, copper powder as well as copper salt were found to promote self-decomposition of **1** into N-aryl- or N,N-diaryltosylamides, triarylbismuthine, and tosylamide.



Compound **1a**, previously described as a moisture-sensitive solid,[1)] failed to appear as such in spite of many attempts. Our syrupy product, when left to stand in air, gradually turned into a solid, major components of which were triphenylbismuthine, its oxide, tosylamide, and bismuth-containing polymeric powder. Thus, a "bismuthimine **1a**" reported by Wittig and coworker[1)] was likely to be a mixture of triphenylbismuth oxide and some other decomposition products from **1a**. Triphenylbismuth oxide was converted into pentaphenylbismuth by treatment with excess phenyllithium and this behavior is in accord with the reported property of "**1a**", on which structural assignment was made by the previous workers. On a similar treatment, our product failed to produce pentaphenylbismuth.

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7) A representative procedure is as follows. To a suspension of chloramine-T (0.32 g, 1.4 mmol) in dry acetonitrile (20 ml) was added triphenylbismuthine (0.44 g, 1 mmol) and the mixture was heated at 75-80 °C with stirring under argon. The color of the suspension gradually turned yellow. After 3 h the mixture was cooled to room temperature and freed from the precipitated NaCl and unchanged chloramine-T. A yellowish filtrate was concentrated under reduced pressure and the residue was left in vacuo for 3 h to give a pale orange syrupy oil **1a** almost in a quantitative yield. Similarly, bismuthimines **1b-d** were obtained as a glassy mass (**1b,c**) or a syrupy oil (**1d**) in nearly quantitative yields. Prolonged heating of the reaction mixture led to decrease in yields of bismuthimines and extensive formation of bismuth-containing polymeric powder. Neither attempts to crystallize the bismuthimines from a variety of organic solvents nor to purify them by column chromatography were successful.

8) Commercial chloramine-T was dehydrated and dried under vacuum prior to use. Hydrated reagent gave the same product, although the formation of side products became rather prominent.

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