

ORGANOBISMUTH COMPOUNDS

V*. PREPARATION, CHARACTERIZATION, AND PROPERTIES OF TRIPHENYLBISMUTH DIAZIDE AND DICYANIDE

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SUMMARY

Triphenylbismuth diazide and the dicyanide have been prepared and characterized. Previously reported triphenylbismuth hydroxide cyanide has been shown to be triphenylbismuth dicyanide. A trigonal bipyramidal structure is indicated for both the compounds on the basis of their infrared and laser Raman spectra. The molecular weight and conductance data for the diazide in acetone are also in accord with a molecular structure. The dicyanide is, however, decomposed in solution into diphenylbismuth cyanide and benzonitrile. Thermal decomposition of the solid dicyanide and the diazide has also been studied. The possibility of the conversion of the diazide and the dicyanide into the corresponding dicyanate has been explored. Unlike transition metal azides, the triphenylbismuth diazide does not react with CO. Triphenylbismuth dicyanide could also not be converted into the corresponding dicyanate by reaction with either HgO or MnO₂. Reaction with HgO afforded triphenylbismuth oxide and the reaction with MnO₂ gave uncharacterized products.

INTRODUCTION

Triphenylbismuth pseudohalides, Ph₃BiX₂, were first reported by Challenger and co-workers. These workers prepared triphenylbismuth dicyanate¹ and the diazide² but found that the corresponding dicyanide^{1,3}, dithiocyanate^{1,3} or the diselenocyanate⁴ could not be isolated. Triphenylbismuth diazide was reported² to decompose at 100° into diphenylbismuth azide and phenyl azide. In a recent study⁵, however, the preparation of diphenylbismuth azide by the thermal decomposition of triphenylbismuth diazide has been questioned, but no data have been reported on the characterization of the triphenylbismuth diazide used for the thermal decomposition. During the past decade a number of organometallic azides⁶⁻⁸ have been prepared and characterized. Although triphenylbismuth diazide is one of the first reported organometallic azides, it has hitherto not been characterized by any physical method.

Challenger and Richards² also reported triphenylbismuth hydroxide cyanide.

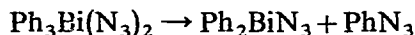
* For Part IV, see ref. 12.

Although analogous hydroxide chloride⁹ and hydroxide bromide⁹ have also been reported, in view of the results of recent studies on several triorgano-antimony(V)^{10,11} and -bismuth(V)¹² derivatives, the existence of the hydroxide derivatives is open to question. Continuing our studies¹² on organobismuth compounds, we have investigated the preparation and properties of triphenylbismuth pseudohalides. The preparation and characterization of triphenylbismuth dicyanate has been reported in a previous publication¹³. In this paper we report on the preparation, characterization and some properties of triphenylbismuth diazide and the dicyanide.

RESULTS AND DISCUSSION

As reported by Challenger and Richards², the reaction of triphenylbismuth dichloride with aqueous sodium azide afforded white crystalline triphenylbismuth diazide, but it was found necessary to carry out the reaction and crystallization at a lower temperature ($\approx 5^\circ$). A white crystalline compound, similar to that described by Challenger and Richards as triphenylbismuth hydroxide cyanide², was also isolated from the reaction with aqueous potassium cyanide. However, the analytical and spectroscopic data indicate it to be triphenylbismuth dicyanide. Challenger and Richards² found that benzonitrile, triphenylbismuth and cyanogen were formed when the so called hydroxide cyanide was steam distilled. Steam distillation of the dicyanide also gave similar products. Thus, there seems little doubt that the product which Challenger and Richards² formulated as triphenylbismuth hydroxide cyanide was in fact triphenylbismuth dicyanide. The isolation of triphenylbismuth diazide and dicyanide from aqueous medium is remarkable since analogous antimony diazide¹⁰ is readily hydrolyzed in the presence of moisture and the analogous dicyanide¹⁰ has yet not been isolated due to its hydrolytic instability.

Triphenylbismuth diazide decomposes slowly at room temperature as shown by the infrared spectral and analytical data. Contrary to the recently reported study⁵, diphenylbismuth azide and triphenylbismuth were obtained in good yield when the solid diazide was heated to 100° . Thus, as reported by Challenger and Richards², the thermal decomposition of the diazide can be represented by the following equation.



Triphenylbismuth is formed upon subsequent decomposition of diphenylbismuth azide. Significant decomposition of the dicyanide was not indicated at room temperature. Samples of the white dicyanide became light brown when heated up to 60° , for 24 h, but no change was observed in the infrared spectrum. A large amount of an uncharacterized material and a small amount of diphenylbismuth cyanide were obtained when the dicyanide was heated at 80° for about 18 h or at 100° for about an hour. Complete cleavage of the Bi-Ph and Bi-CN bonds occurred, and cyanogen was evolved when the dicyanide was heated at 140° .

Both the diazide and dicyanide are soluble in common organic solvents, except petroleum ethers. However, in solution, the dicyanide is decomposed into diphenylbismuth cyanide and benzonitrile. In acetone, a molecular weight of 531 was obtained for the diazide (mol. wt. calcd., 524), whereas for the dicyanide the value was 285 (mol. wt. calcd., 483). Since, molar conductances for $1.85 \times 10^{-3} M$ solutions of these compounds, in acetone, were 0.28 and $0.83 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, respectively

the possibility of an ionic dissociation can be ruled out. A solution of the dicyanide in 95% alcohol turned yellow in about an hour and after 24 h afforded crystals of diphenylbismuth cyanide. The infrared spectrum of the mother liquor indicated the presence of benzonitrile. A similar but slower decomposition was observed in benzene or chloroform. The diazide does not appear to decompose in a similar manner. Over a period of 24 h, a small amount of an uncharacterized light brown solid was precipitated from a chloroform solution of the diazide which did not contain any diphenylbismuth azide. The solution afforded mostly undecomposed diazide and a small amount of triphenylbismuth.

Important infrared and Raman frequencies for the diazide and the dicyanide are recorded in Table 1. For either compound no bands were observed which could be attributed to the O-H¹⁴ or the Bi-O-Bi¹² stretching frequencies. The infrared and Raman bands due to the Ph₃Bi group for both the compounds were almost identical to those observed for other Ph₃BiX₂^{13,15} derivatives and will not be discussed here. Most of the assignments presented in Table 1 follow from those established in the literature^{6,7,14,16}. The assignments for the Bi-N₃ and Bi-CN stretching frequencies are consistent with the Bi-X frequencies for other Ph₃BiX₂ derivatives¹⁵. The infrared and Raman spectra for both the compounds are, thus, in accord with a trigonal-bipyramidal structure which has been established for triphenylbismuth dichloride, by X-ray diffraction studies¹⁷.

Attempts to convert either the diazide or the dicyanide into dicyanate were unsuccessful. Azido complexes¹⁸ of platinum group metals readily react with CO to form the corresponding isocyanato complexes. No reaction occurred when CO was passed for 3 h through a chloroform solution of the diazide. As observed for organosilicon(IV) cyanides¹⁹, the reaction of triphenylbismuth dicyanide and HgO in chloroform resulted in the formation of triphenylbismuth oxide and mercuric cyanide. However, in contrast to the formation of organosilicon(IV) isocyanates from the

TABLE 1

ANALYTICAL DATA AND INFRARED AND RAMAN SPECTROSCOPIC
Frequencies^a for triphenylbismuth diazide and dicyanide

Compound	M.p. (°C)	Analysis found (calcd.) (%)			Frequency (cm ⁻¹)	Assignment				
		C	H	N						
Ph ₃ Bi(N ₃) ₂	95 ^b	41.38	2.92	15.73	IR 2050 s, 2040 s 2063 s ^c R 2047 mw, 2034 mw IR 1315, 1315 ^d m 1265, 1265 ^d ms IR 303 ms, 298 ^d s R 328 ms	} ν_{as} (NNN) 2 δ (NNN) ν_s (NNN) ν_{as} (Bi-N ₃) ν_s (Bi-N ₃)				
		(41.23)	(2.88)	(16.02)						
		Ph ₃ Bi(CN) ₂	134 ^b	48.37			3.22	5.81	IR 2135 mw, 2128 mw 2140 ^c m R 2136 m IR 275 m R 289 mw	} ν (CN) ν_{as} (Bi-CN) ν_s (Bi-CN)
				(48.79)			(3.07)	(5.68)		

^a In the solid state unless stated otherwise; ^b Decomposed on melting; ^c In CHCl₃; ^d In benzene; m, medium; s, strong; w, weak.

reaction²⁰ of organosilicon(IV) cyanides with MnO_2 , an intractable product was obtained by the reaction of triphenylbismuth dicyanide with MnO_2 at 40° . Complete decomposition of the dicyanide occurred when the reaction was carried out at 100° .

EXPERIMENTAL

General

Triphenylbismuth dichloride was prepared as described previously¹³. Other solvents and chemicals were reagent grade and were used without further purification. Elemental analyses were performed at Uniroyal Research Laboratory, Guelph, and the analytical data are collected in Table 1. Raman spectra were obtained on a Spex Model 1400 spectrometer using the 6328 Å line of a helium/neon laser as the exciting frequency. Infrared spectra, electrical conductivities and molecular weights were measured as described previously¹¹. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected.

Preparation of triphenylbismuth diazide and dicyanide

Triphenylbismuth dichloride (0.01 mol) and sodium azide or potassium cyanide (0.04 mol) were mixed in 20 ml cold water and the mixture was shaken on a cold plate ($\approx 5^\circ$) for 8 h. The solid was then filtered and washed with ice-cold water until it was free from the alkali metal salt. Upon crystallizing the solid three times from an ice-cold mixture of chloroform and petroleum ether (b.p. $35\text{--}60^\circ$), a white crystalline product was obtained which was stored in a refrigerator.

Decomposition of solid triphenylbismuth diazide

When 1 g of the diazide was heated to 100° , a pasty mass with a strong odour of phenyl azide was formed. Extraction with cold light petroleum yielded triphenylbismuth; the residue with hot alcohol gave crystals of diphenylbismuth azide which melted at 168° and showed azide bands at 2048, 1265 and 655 cm^{-1} .

Decomposition of triphenylbismuth diazide in chloroform

Triphenylbismuth diazide ($\approx 1\text{ g}$) was dissolved in chloroform and the solution was kept at room temperature for 24 h. A brown precipitate was formed which was filtered. The infrared spectrum of the precipitate showed a strong band at 2060 and a medium band at 2130 cm^{-1} but did not show bands due to triphenyl- or diphenylbismuth groups. Undecomposed diazide and a very small amount of triphenylbismuth were recovered from the filtrate.

Steam distillation of triphenylbismuth dicyanide

About 2 g triphenylbismuth dicyanide was steam distilled for about 3 h. The distillate ($\approx 400\text{ ml}$) was shaken with diethyl ether and the water layer was separated. Upon adding silver nitrate to the water layer, silver cyanide was precipitated and was characterized by its infrared spectrum. Evaporation of the ether layer gave a small amount of a thick, viscous, paste-like material which showed infrared bands due to benzonitrile and triphenylbismuth. The residue in the flask was filtered off, and dried at room temperature. Upon treating it with light petroleum ether, triphenylbismuth and small amount of an uncharacterized inorganic material were obtained.

Decomposition of triphenylbismuth dicyanide in alcohol, benzene and chloroform

In a typical experiment, 1 g of triphenylbismuth dicyanide was dissolved in about 20 ml 95% ethanol. The solution turned yellow in about an hour and upon keeping the solution at room temperature for 24 h crystals of diphenylbismuth cyanide were deposited, which were filtered off and dried at room temperature. The melting point and the infrared spectrum of the crystals were identical to those for an authentic sample of diphenylbismuth cyanide. The infrared spectrum of the supernatant liquid showed the presence of benzonitrile. Upon evaporating the supernatant liquid some triphenylbismuth was obtained. The decomposition in benzene or chloroform was studied in a similar manner.

Thermal decomposition of solid triphenylbismuth dicyanide

(a). Samples of the solid dicyanide (0.5 g) were heated at 40° and 60° respectively for 24 h. Both the samples turned light brown but no change was observed in the infrared spectrum of either sample. The dicyanide (0.6 g) was heated at 80° and the infrared spectrum of the solid was recorded after every four hours. The sample turned brown and the intensity of the 2136 cm^{-1} band gradually diminished and an additional band appeared at ca. 2180 cm^{-1} . After 18 h the sample became dark brown and its infrared spectrum did not show the 2136 cm^{-1} band. Treatment of the solid with benzene gave a residue which upon treatment with alcohol afforded diphenylbismuth cyanide ($\approx 0.1\text{ g}$) and some uncharacterized inorganic material. The benzene soluble portion afforded an uncharacterized material (0.05 g) which showed characteristic phenyl bands and a band of medium intensity at 2180 cm^{-1} . Similar results were obtained by heating a sample at 100°.

(b). About 1 g of triphenylbismuth dicyanide was placed in a 100 ml round bottom flask equipped with a gas outlet tube. The flask was heated in an oil bath. When the temperature of the bath reached 140°, cyanogen was evolved and it was bubbled through an aqueous solution of silver nitrate. The precipitated silver cyanide was filtered off and characterized by its infrared spectrum. The infrared spectrum of the residue left in the distillation flask did not show the presence of any organobismuth species.

Reaction of triphenylbismuth dicyanide with HgO

A solution of triphenylbismuth dicyanide (0.2 g) in chloroform (15 ml) was stirred with mercuric oxide for an hour, at room temperature. The mixture was filtered. Evaporation of the filtrate to dryness afforded triphenylbismuth oxide which was characterized by its infrared spectrum. The residue was dissolved in hot ethanol, filtered and the filtrate was evaporated to dryness to give a white solid. The infrared spectrum of the white solid was identical with that of an authentic sample of mercuric cyanide.

Reaction of triphenylbismuth dicyanide with MnO₂

Triphenylbismuth dicyanide was mixed with an excess of MnO₂ and the mixture was kept at 40° for 48 h. Treatment of the mixture with chloroform or benzene and subsequent evaporation of the solution afforded an uncharacterized product which did not contain any triphenylbismuth dicyanate. When a mixture of the dicyanide and MnO₂ was heated at $\approx 100^\circ$ fumes were evolved. No organobismuth species could be detected in the residue left in the test tube.

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