

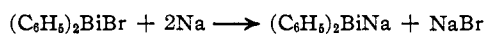
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactions of Organobismuth Compounds in Liquid Ammonia

BY HENRY GILMAN AND H. L. YABLUNKY

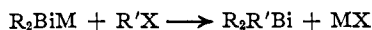
This paper describes the preparation and reactions of new types of organobismuth compounds in liquid ammonia.

Diarylbismuth Metallic Compounds.—Diarylbismuth halides react smoothly with metals which dissolve in liquid ammonia to give deep red R_2BiM compounds.



The metals examined have been lithium, sodium, potassium, calcium and barium. Studies on related reactions with organolead halides indicate that the alkaline earth metals may function in a monovalent stage¹; however, the investigations with organobismuth compounds show the alkaline earth metals to function definitely in these particular reactions in the normal divalent state.

The R_2BiM compounds decompose slowly to the corresponding R_3Bi compound and inorganic bismuth, but they are sufficiently stable to react promptly with RX compounds. This provides an additional avenue of approach (see preceding paper²) to unsymmetrical organobismuth compounds.

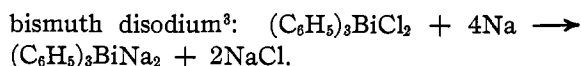


Here, again,² reaction is impeded or excluded with some $R'X$ compounds having a radical with steric hindrance characteristics. The high reactivity of the R_2BiM compounds is due in part to their solubility in liquid ammonia, for the insoluble sodium-bismuth alloy did not react with iodobenzene.

Cleavage by Sodium.—One approach to the preparation of an organobismuth compound that would lend itself to studies on optical isomerism is illustrated by the following reactions.



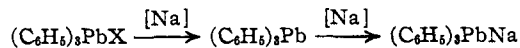
However, although reaction takes place between triphenylbismuth and sodium, there is no evidence for the appreciable formation of an R_2BiNa compound. There is a possibility that sodium may have added to give a compound like R_3BiNa_2 , but reaction of triphenylbismuth dichloride and sodium provided no indication of a triphenyl-



Another type of organobismuth sodium compound may have formed in the attempted cleavage of R_3Bi by sodium, namely, $RBiNa_2$. However, an attempt to prepare a compound of this kind by another procedure was unsuccessful. When α -naphthylbismuth dibromide was treated with four equivalents of sodium and then with iodobenzene, none of the readily identifiable diphenyl- α -naphthylbismuth was isolated: α - $C_{10}H_7BiBr_2 \xrightarrow{[4Na]} \alpha$ - $C_{10}H_7BiNa_2 \xrightarrow{[C_6H_5I]} \alpha$ - $C_{10}H_7Bi(C_6H_5)_2$. Instead, the iodobenzene was recovered quantitatively, and the yield of naphthalene was 27.4%. The recovery of iodobenzene indicates the absence of any free sodium, for iodobenzene and sodium in liquid ammonia yield benzene, diphenylamine and triphenylamine.⁴

Possible Formation of Diphenylbismuth.—There is evidence for the transient existence of dimethylbismuth and diethylbismuth.⁵ Inasmuch as several organometallic radicals⁶ have been prepared by the following general reaction, $R_2MX_2 + Na \cdot Hg \longrightarrow R_2M + 2NaX$, we treated diphenylbismuth halides with one equivalent of lithium, sodium, potassium, calcium or barium to effect this reaction: $(C_6H_5)_2BiX + Na \longrightarrow (C_6H_5)_2Bi + NaX$.

The only present evidence for the intermediate formation of diphenylbismuth (or tetraphenylbismuth) was an intense green color. This color, which gives way to the characteristic deep red color of diphenylbismuth sodium when more sodium is added, is a satisfactory indication of diphenylbismuth if one may draw analogies with the closely related organolead compounds. For example, the following reactions can be effected stepwise in liquid ammonia.⁷



(3) On theoretical grounds, based on the aquo-system, such a compound would be extremely unstable: Birchenback and Kellermann, *Ber.*, **58**, 786, 2377 (1925); Challenger and Wilson, *J. Chem. Soc.*, 209 (1927).

(4) White, *THIS JOURNAL*, **45**, 779 (1923).

(5) Denham, *ibid.*, **43**, 2367 (1921); Paneth and co-workers, *Ber.*, **62**, 1335 (1929); *J. Chem. Soc.*, 366 (1935).

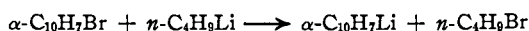
(6) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 478.

(7) Gilman and Bailie, *THIS JOURNAL*, **61**, 731 (1939). See also Calingaert and Soroos, *J. Org. Chem.*, **2**, 535 (1938).

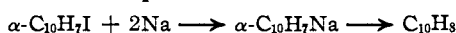
(1) By R. Leeper.

(2) Gilman and Yablunky, *THIS JOURNAL*, **63**, 207 (1941).

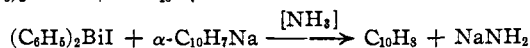
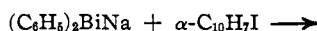
Halogen-Metal Interconversion.—The following reaction is typical of numerous halogen-metal interconversion reactions where both the halogen and the metal are attached to carbon.⁸



A related reaction appears to take place between diphenylbismuth metallic compounds and α -iodonaphthalene in liquid ammonia. In these reactions, where the M in $(\text{C}_6\text{H}_5)_2\text{BiM}$ is lithium, sodium, potassium, calcium or barium, significant quantities (up to 34.6%) of naphthalene are formed in addition to the diphenyl- α -naphthylbismuth. The naphthalene very probably does not come from the following reaction which we have shown to proceed to the extent of 47%



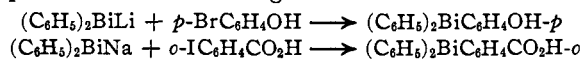
for there is no free sodium in the diphenylbismuth sodium solutions. A slight excess of sodium over that required to form diphenylbismuth sodium changes the color of the solution from the deep red of R_2BiM to a dark blue characteristic of the metal dissolved in liquid ammonia. It appears, therefore, that the naphthalene may owe its formation to a new type of halogen-metal interconversion reaction.



A related explanation may be valid for the formation of triphenylbismuth (20%) as one of the products in a reaction between diphenylbismuth sodium and α -iodonaphthalene, for we have shown that diphenylbismuth iodide in liquid ammonia is converted spontaneously to triphenylbismuth.

Water-Soluble Organobismuth Compounds.—

The liquid ammonia reactions of R_2BiM compounds provide another⁹ avenue of approach to the preparation of water-soluble organobismuth compounds. The following reactions were examined.



Evidence is presented indicating the formation of each of these compounds: the phenolic compound being rather unstable as might have been expected because of the lability of an hydroxyphenyl radical attached to a metal; and the impure benzoic acid derivative being soluble. We have already mentioned that three products have been

(8) Gilman and Moore, *THIS JOURNAL*, **62**, 1843 (1940).

(9) See the preceding paper for tri-*p*-dimethylaminophenylbismuth. Also, Gilman and Svigoon, *ibid.*, **61**, 3586 (1939); and Gilman and Yablunsky, *ibid.*, **62**, 665 (1940).

isolated from the related interaction of diphenylbismuth sodium and α -iodonaphthalene. Variations in experimental procedures may give more of the direct coupling product which would facilitate the isolation of water-soluble types in appreciable quantities.

Incidental to this phase of the study, we observed that halogens which are *ortho* or *para* to the functional group in benzoic acid or benzoates appear to be less reactive in liquid ammonia with R_2BiNa than the halogen in a simple halogenated benzene or naphthalene. The halogen in *m*-bromobenzoic acid did not react at all under comparable conditions.

Relative Stabilities of Diphenylbismuth Halides in Liquid Ammonia.—Extensive studies¹⁰ of compounds like $(\text{C}_6\text{H}_5)_3\text{BiX}_2$ have shown that the order of decreasing stability of the dihalides is: R_3BiCl_2 , R_3BiBr_2 , R_3BiI_2 . With R_2BiX types in liquid ammonia, the order appears to be reversed. The preparation of diphenylbismuth chloride and diphenylbismuth bromide must be carried out under strictly anhydrous conditions to avoid decomposition. On the other hand, the preparation of diphenylbismuth iodide involves pouring an absolute ethanol solution of the compound into boiling water; and the yields, in excess of 60%, belie any profound hydrolysis. Also, diphenylbismuth iodide is ammonolyzed to the extent of 30% by liquid ammonia; under similar conditions, diphenylbismuth bromide is 62% ammonolyzed; and the insolubility of diphenylbismuth chloride did not lend itself to a comparative study. Indirect evidence for the prompt ammonolysis of diphenylbismuth chloride is recorded in the Experimental Part in a reaction between diphenylbismuth chloride and an insufficient quantity of sodium.

Another illustration of the greater reactivity of diphenylbismuth chloride over the corresponding iodide may be the reduction reaction with hydrazine. Diphenylbismuth chloride is instantaneously converted by hydrazine to triphenylbismuth in 93.5% yield; under similar conditions, diphenylbismuth iodide¹¹ gives but a 61.2% yield of triphenylbismuth after eight hours.

Experimental Part

Diphenylbismuth Sodium.—Using a three-necked flask provided with a mechanical stirrer, 2.45 g. (0.005 mole)

(10) Challenger and Richards, *J. Chem. Soc.*, 405 (1934).

(11) The results with diphenylbismuth iodide are not recorded in the paper by Gilman and Yablunsky, *THIS JOURNAL*, **62**, 665 (1940).

of diphenylbismuth iodide was dissolved in 150 cc. of liquid ammonia. To the stirred solution was added gradually 0.23 g. (0.01 g. atom) of sodium. When nearly one-half of the sodium had been added the solution became green; and as more sodium was added the color gradually became red, and finally was deep dark red.

If the solution was allowed to decompose spontaneously, a yield of 0.72 g. (49.1%) of triphenylbismuth was obtained.

On the addition to the diphenylbismuth sodium solution of 1.27 g. (0.005 mole) of α -iodonaphthalene in 10 cc. of dry ether, the red color was discharged instantly, and evaporation of the ammonia gave a residue from which was isolated three compounds: 0.6 g. (24.5%) of diphenyl- α -naphthylbismuth; 0.22 g. (34.6%) of naphthalene; and 0.3 g. (20.5%) of triphenylbismuth. Each of these products was identified by the method of mixed melting points. None of the naphthalene was contained in the α -iodonaphthalene which was freshly distilled.

Apparently no appreciable amount of diphenylbismuth sodium is formed when the diphenylbismuth iodide is added to the solution of the metal in liquid ammonia.

If diphenylbismuth bromide is used in place of the corresponding iodide, the yield of diphenyl- α -naphthylbismuth is 40.8%, and the yield of naphthalene is 15.8%.

When diphenylbismuth chloride is used together with 1.73 equivalents of sodium, the yield of diphenyl- α -naphthylbismuth is 30.6%. The use of two equivalents of sodium gave, subsequent to treatment with α -iodonaphthalene, a 42.8% yield of triphenylbismuth which contained a small quantity of diphenyl- α -naphthylbismuth as impurity. An explanation of these two unusual reactions probably lies in the rapid ammonolysis of diphenylbismuth chloride. It is evident that approximately 13.5% of the sodium is in excess in the second reaction, indicating that a corresponding amount of diphenylbismuth chloride is unavailable for reaction. This excess of metal must then react in such a way as to convert the diphenylbismuth sodium already formed to triphenylbismuth, and leave only a small part of the former compound available for interaction with α -iodonaphthalene.

Diphenylbismuth Lithium, -Potassium, -Calcium and -Barium.—These $(C_6H_5)_2BiM$ compounds were prepared in accordance with the directions given for diphenylbismuth sodium, using a quantity of metal equivalent to the sodium. Each of these solutions in liquid ammonia was treated with α -iodonaphthalene, and Table I gives the percentage yields of diphenyl- α -naphthylbismuth and naphthalene.

TABLE I
REACTIONS BETWEEN $(C_6H_5)_2BiM$ AND α -IODONAPHTHALENE

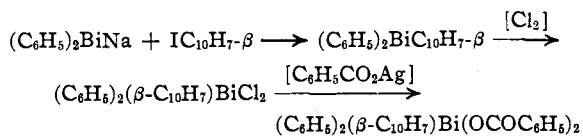
M in $(C_6H_5)_2BiM$ or in $[(C_6H_5)_2Bi]_2M$	$(C_6H_5)_2BiC_{10}H_7-\alpha$, %	$C_{10}H_8$, %
Li	24.5	6.3
Na	24.5	34.6
K	24.5	31.5
Ca	4.1	26.8
Ba	10.0	20.6

Di-*p*-tolyl- α -naphthylbismuth.—From 2.5 g. (0.005 mole) of di-*p*-tolylbismuth iodide, 150 cc. of liquid am-

monia, 0.23 g. (0.01 g. atom) of sodium, and 1.27 g. (0.005 mole) of α -iodonaphthalene in 10 cc. of ether there was obtained 0.5 g. (19.3%) of di-*p*-tolyl- α -naphthylbismuth melting at 129–130°. This product was shown to be identical by a series of mixed melting points with the two different preparations of di-*p*-tolyl- α -naphthylbismuth described in the preceding paper.

Di-*p*-chlorophenyl- α -naphthylbismuth.—To the dark red solution of di-*p*-chlorophenylbismuth sodium prepared from 2.8 g. (0.005 mole) of di-*p*-chlorophenylbismuth iodide, 0.23 g. (0.01 g. atom) of sodium, and 150 cc. of liquid ammonia was added 1.27 g. of α -iodonaphthalene in 10 cc. of ether. After working up the reaction mixture in the usual manner, there was obtained 0.3 g. (10.8%) of di-*p*-chlorophenyl- α -naphthylbismuth. The melting point and mixed melting points with the two different preparations of di-*p*-chlorophenyl- α -naphthylbismuth described in the preceding paper was 136–137°.

Diphenylbismuth Sodium and β -Iodonaphthalene.—The cherry-red color of diphenylbismuth sodium prepared from 2.45 g. (0.005 mole) of diphenylbismuth iodide and 0.23 g. (0.01 g. atom) of sodium in 150 cc. of liquid ammonia turned black on the addition of 1.3 g. (0.005 mole) of β -iodonaphthalene in 50 cc. of ether. The residue remaining after the ammonia was evaporated was extracted with chloroform; the chloroform was then removed under reduced pressure, and methanol was added. Prolonged cooling did not effect crystallization of the expected diphenyl- β -naphthylbismuth. Accordingly, the oil was dissolved in dry chloroform and treated with gaseous chlorine to form the corresponding dichloride. However, the dichloride was also obtained as an oil, and this was dissolved in chloroform and shaken with one gram of silver benzoate for twenty-four hours. Filtration from silver halide, removal of the solvent, and the addition of methanol gave a solid which after one crystallization from a mixture of chloroform and methanol melted at 138–140°. The following reactions illustrate the several transformations culminating in the formation of diphenyl- β -naphthylbismuth dibenzoate.



Anal. Calcd. for $C_{36}H_{27}O_4Bi$: Bi, 28.55. Found: Bi, 28.30 and 28.69.

Diphenylbismuth Sodium and *p*-Iodobiphenyl.—To 0.005 mole of diphenylbismuth sodium in 100 cc. of liquid ammonia was added 1.4 g. (0.005 mole) of *p*-iodobiphenyl in 25 cc. of ether. The typical change from red to black was observed. The residue remaining after evaporation of the ammonia was extracted with chloroform; and an oil remained after removal of the chloroform; the addition of methanol, and cooling. The oil (in chloroform) was treated with chlorine, but the dichloride resisted crystallization. Then in accordance with the procedures described in the preceding section, the dichloride was treated with silver benzoate to give diphenyl-*p*-biphenylbismuth dibenzoate. Crystallization from a chloroform-methanol mixture gave small yellowish crystals which grind to a

white powder melting at 145–147°, free of halogen, and which depresses the melting point of triphenylbismuth dibenzoate.

Anal. Calcd. for $C_{88}H_{29}O_4Bi$: Bi, 27.57. Found: Bi, 27.45 and 27.75.

Diphenylbismuth Sodium and *p*-Bromodimethylaniline.—A solution of diphenylbismuth sodium in liquid ammonia, prepared from 2.45 g. (0.005 mole) of diphenylbismuth iodide, was treated with 1.2 g. (0.006 mole) of *p*-bromodimethylaniline in 50 cc. of ether. After evaporation of the ammonia, the residue was extracted with chloroform and the chloroform then removed under reduced pressure. The addition of 20 cc. of methanol gave colorless crystals melting at 179° and these after crystallization from chloroform–methanol melted at 187°.

Anal. Calcd. for $C_{20}H_{29}NBi$: Bi, 43.27. Found: Bi, 52.33.

This product is to be investigated further. From the original methanol filtrate were recovered 0.38 g. of triphenylbismuth and 0.47 g. of unreacted *p*-bromodimethylaniline.

Triphenylbismuth from Diphenylbismuth Sodium and Some Aryl Halides.—The formation of triphenylbismuth described in the preceding section has been noted in quite appreciable quantities in other related reactions. To the red solution of diphenylbismuth sodium in liquid ammonia [prepared from 2.45 g. (0.005 mole) of diphenylbismuth iodide] was added with stirring 1.2 g. (0.0075 mole) of bromobenzene in 25 cc. of dry ether. The red color was discharged immediately. Stirring was continued for one hour; the ammonia was allowed to evaporate spontaneously; and from the residue was isolated 1.46 g. (66.3%) of triphenylbismuth.

From a corresponding reaction in which iodobenzene was used, the yield of triphenylbismuth was 57.9%; and from a reaction with *o*-bromoanisole, the yield of triphenylbismuth was 59%.

A reaction between 0.005 mole of diphenylbismuth sodium and 1.24 g. (0.005 mole) of *o*-iododimethylaniline gave an oil which, because it resisted crystallization, was dissolved in chloroform and then treated with chlorine. Partial evaporation of the solvent and the addition of several volumes of methanol gave 0.8 g. (47.1%) of triphenylbismuth dichloride (mixed melting point).

From 0.005 mole of diphenylbismuth sodium and 1.34 g. (0.0064 mole) of α -bromonaphthalene there was obtained 0.52 g. (35.2%) of triphenylbismuth, identified as the dichloride. There was no evidence of the formation of the unsymmetrical diphenyl- α -naphthylbismuth.

α -Naphthylbismuth Dibromide and Sodium.—The addition of 0.53 g. (0.0228 g. atom) of sodium to 2.85 g. (0.0057 mole) of α -naphthylbismuth dibromide in 150 cc. of liquid ammonia resulted first in the formation of a milky white solution which turned black as more of the sodium metal was added. The subsequent addition of 2.33 g. (0.0114 mole) of iodobenzene in 25 cc. of dry ether caused no visible reaction. After evaporation of the ammonia, the residue was extracted with chloroform; the chloroform was then removed to give an oil which contained no diphenyl- α -naphthylbismuth but which yielded on steam distillation a quantitative recovery of iodobenzene (identified as its

nitro derivative¹²), together with 0.2 g. (27.4%) of naphthalene.

Sodium–Bismuth Alloy and Iodobenzene.—The preparation of sodium–bismuth alloy was patterned after the directions of Kraus and Kurtz.¹³ To a solution of 1.45 g. (0.063 g. atom) of sodium in 150 cc. of liquid ammonia was added with stirring 3.15 g. (0.01 mole) of anhydrous bismuth chloride in small portions. The reaction was very vigorous and the blue color of the sodium disappeared when nearly all of the bismuth chloride had been added. There was then added 6.12 g. (0.03 mole) of iodobenzene. After most of the ammonia had evaporated, a small quantity of ammonium chloride was added. On working up the products in the usual manner, there was recovered 2 g. of iodobenzene together with some resinous material which could not be distilled and which was free of bismuth.

In another experiment, the reaction was allowed to proceed for twelve hours by the repeated addition of liquid ammonia. There was recovered 1 g. of iodobenzene but no triphenylbismuth, and the inorganic bismuth residue weighed 3.15 g.

Triphenylbismuth and Sodium.—To a solution of 2.2 g. (0.005 mole) of triphenylbismuth in 50 cc. of dry ether was added slowly 100 cc. of liquid ammonia. The triphenylbismuth precipitated as a fluffy solid. The deep red solution which formed on the gradual addition of 0.23 g. (0.01 g. atom) of sodium was filtered¹⁴ through glass wool in an atmosphere of ammonia. To this rapidly stirred solution was added 1.27 g. (0.005 mole) of α -iodonaphthalene in ether. There was isolated 0.49 g. (77.2%) of naphthalene, 0.4 g. (18.2%) of triphenylbismuth, but no diphenyl- α -naphthylbismuth. It will be noted that the yield of naphthalene is distinctly higher in this experiment than in the reaction described later between only α -iodonaphthalene and sodium. This indicates some sort of unusual reactivity of the sodium.

Triphenylbismuth Dichloride and Sodium.—Liquid ammonia itself reduces triphenylbismuth dichloride to triphenylbismuth in about 10% yields. When the dichloride in liquid ammonia was treated with 4 equivalents of sodium, a deep red solution was formed. The addition of α -iodonaphthalene discharged the red color. The yield of naphthalene was 71%, and that of triphenylbismuth, 12.3%. The high yield of naphthalene again indicates an unusual reactivity of the sodium (see the following experiment).

α -Iodonaphthalene and Sodium.—To a solution of 0.23 g. of sodium in 100 cc. of ammonia was added 1.27 g. of α -iodonaphthalene in 10 cc. of ether. The yield of naphthalene was 0.3 g. (47.2%).

Diphenylbismuth Lithium and *p*-Bromophenol.—A reaction was carried out between diphenylbismuth lithium (prepared from 2.45 g. of diphenylbismuth iodide in 150 cc. of liquid ammonia and 0.07 g. of lithium) and 0.87 g. (0.005 mole) of *p*-bromophenol in 10 cc. of ether. On

(12) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935, p. 83.

(13) Kraus and Kurtz, THIS JOURNAL, 47, 43 (1925).

(14) In studies on organolead compounds, Mr. Bindschadler has found that this filtration removes much of the sodamide formed in the

reaction: $(C_6H_5)_4Pb + 2Na \xrightarrow{[NH_3]} (C_6H_5)_3PbNa + C_6H_5Na \xrightarrow{C_6H_5 + NaNH_2} C_6H_5 + NaNH_2$. The sodamide interferes with the subsequent coupling reaction with RX compounds.

working up in a customary manner there were obtained 0.66 g. of triphenylbismuth, and 0.15 g. of a product which melted at 179–180° (with prior shrinking) after crystallization from chloroform–methanol.

Anal. Calcd. for $C_{16}H_{15}OBi$: Bi, 45.83. Found: Bi, 40.98.

The chloroform–methanol filtrate (from which was obtained the product melting at 179–180°) deposited, on standing, triphenylbismuth. Apparently, the expected diphenyl-*p*-hydroxyphenylbismuth is very unstable.

Diphenylbismuth Sodium and Halogenated Benzoic Acids.—Addition of 1.24 g. (0.005 mole) of *o*-iodobenzoic acid in ether to 0.005 mole of diphenylbismuth sodium discharged the red color. In addition to 0.95 g. (65%) of triphenylbismuth, there was obtained an alkali soluble compound which contained bismuth. This as yet unidentified product melted at 152° with shrinking at 145°.

From a corresponding reaction with *m*-bromobenzoic acid there was obtained a 75.3% yield of triphenylbismuth and a quantitative recovery of *m*-bromobenzoic acid.

From a reaction with methyl *p*-bromobenzoate, the only product identified was *p*-bromobenzoic acid. A mixture, soluble in alkali and containing bismuth, has not been resolved.

From a reaction with sodium *o*-iodobenzoate there was obtained a 42.5% yield of triphenylbismuth, and 0.65 g. of a mixture which was soluble in water and contained bismuth. Some orienting attempts at purification resulted in general decomposition.

A reaction between diphenylbismuth sodium and one-half the required amount of *p*-iodobenzoic acid (previously dissolved in a little liquid ammonia) yielded 24.5% of triphenylbismuth, together with an alkali-soluble, bismuth-containing product.

Diphenylbismuth Iodide and Triphenylmethylsodium.—To a solution of triphenylmethylsodium (prepared from 0.01 mole of triphenylmethane) in 150 cc. of liquid ammonia was added 0.01 mole of diphenylbismuth iodide. The chief product, melting between 57–60° after crystallization from chloroform–methanol, was probably a mixture. (See preceding paper.)

Anal. Calcd. for $(C_6H_5)_2BiC(C_6H_5)_3$: Bi, 34.48. Found: Bi, 24.99 and 24.05.

From a reaction between diphenylbismuth sodium and triphenylchloromethane, triphenylbismuth and triphenylmethane were obtained.

Ammonolysis of Diphenylbismuth Iodide and Bromide.—A solution of 2 g. of freshly prepared diphenylbismuth iodide in 150 cc. of liquid ammonia was stirred as the ammonia evaporated (three hours). From the residue there was obtained 0.27 g. (21%) of triphenylbismuth and 1.3 g. (65%) of unreacted diphenylbismuth iodide.

A corresponding experiment with diphenylbismuth bromide yielded 38.2% of unreacted diphenylbismuth bromide. No triphenylbismuth was isolated subsequent to ammonolysis, and the ether insoluble material appeared to consist mostly of inorganic bismuth.

Summary

Diaryl bismuth halides react in liquid ammonia with equivalent quantities of lithium, sodium, potassium, calcium or barium to give highly reactive, deep red colored R_2BiM compounds. These diaryl bismuth metallic compounds react with $R'X$ compounds to give unsymmetrical organobismuth compounds ($R_2R'Bi$), and a water-soluble type ($R_2BiC_6H_4CO_2H$).

The radical diphenylbismuth is formed transiently in the reaction between diphenylbismuth halides and alkali or alkaline earth metals.

A new type of halogen–metal interconversion appears to be involved in the reaction between diphenylbismuth sodium and α -iodonaphthalene.

The decreasing order of relative reactivities of diaryl bismuth halides is: R_2BiCl , R_2BiBr , R_2BiI . This is a reversal of the stabilities of R_3BiX_2 types.

AMES, IOWA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of Higher *cis* and *trans* Olefins¹

BY KENNETH N. CAMPBELL AND LAWRENCE T. EBY

In recent years there has been considerable interest in the preparation of the pure geometrical isomers of olefins. Most methods of preparing olefins yield a mixture of the two geometrical isomers, but in the case of 2-butene these can be separated by fractional distillation.² As the length of the carbon chain increases, however, the

boiling points of the two forms approach each other, and separation by distillation fails. For this reason attention has been turned to methods of preparation which will yield one form and not the other. Several such methods have been proposed, but they are of limited applicability and do not always give the pure isomers. The *cis* and *trans* forms of 2-butene³ and 2-pentene⁴ have been made from the corresponding *cis* and *trans* α - β un-

(1) Paper XLI on the chemistry of substituted acetylenes and their derivatives; previous paper, *THIS JOURNAL*, **62**, 1798 (1940). Part of the material in this paper was presented before the Organic Division at the Detroit meeting, September, 1940.

(2) Kistiakowsky, *et al.*, *ibid.*, **57**, 876 (1935).

(3) Lucas and Prater, *ibid.*, **59**, 1682 (1937).

(4) Sherrill and Matlack, *ibid.*, **59**, 2134 (1937).