[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Preparation of Organobismuth Compounds from Diazonium Compounds

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The Bart[1] reaction and its modifications have provided the essential means for the synthesis of a wide variety of organic compounds of arsenic and antimony. Unsuccessful attempts were made by others[2] to extend the diazonium reaction to the preparation of organic compounds of bismuth. Recently brief mention was made of the first successful preparation of an R_3Bi compound by means of the diazonium reaction.[3] We are now describing the synthesis of a variety of organobismuth compounds by this procedure, and are presenting evidence for some reaction mechanisms.

Aryldiazonium Chloride–Bismuth Chloride Complexes.—Considerable work has been reported on aryldiazonium chloride–bismuth chloride complexes, but much remains to be done to clarify what appears to be a variable coördination number for bismuth in these complexes. Challenger and Wilkinson[2a] have described benzene- and *p*-toluene-diazonium chloride–bismuth chloride complexes whose analyses (when molecules of water of crystallization are included in the molecular formula) indicate the following general types: $(C_6H_5N_2Cl)_2\cdot BiCl_3$ and $(p\text{-}CH_3C_6H_4N_2Cl)_3\cdot BiCl_3$. Supniewski and Adams[2b] have reported the preparation of $C_6H_5N_2Cl\cdot BiCl_3$. The most complete series of complexes prior to the present work was prepared by Nesmeyanov and co-workers,[4] and it demonstrates again an apparent versatility in the coördination number of bismuth in these compounds. A related study by Charrier[5] is open to some criticism, and neither Nesmeyanov and co-workers[4] nor we have succeeded in repeating the work. Apparently, the most careful work is that reported in a thesis by Ammerlahn.[2c] However, the paucity of experimental detail makes it difficult to follow his laboratory directions, and this is particularly regrettable because of frequent difficulties in obtaining analytically pure diazonium complexes.

From correlations with some inorganic bismuth compounds, one might expect salts of the following hypothetical bismuth acids

$$\begin{array}{ccc} HBiX_4 & H_2BiX_5 & H_3BiX_6 \\ (HX\cdot BiX_3) & (2HX\cdot BiX_3) & (3HX\cdot BiX_3) \end{array}$$

in the bismuth chloride–diazonium chloride series

$$(RN_2X\cdot BiX_3) \qquad (2RN_2X\cdot BiX_3) \qquad (3RN_2X\cdot BiX_3)$$

Examples of all three types have been reported. Of the nineteen bismuth chloride complexes described in this study, fifteen have the structure $(RN_2Cl)_2\cdot BiCl_3$. This ratio of diazonium chloride to bismuth chloride occurs in many cases where the quantities of reactants made possible the formation of $RN_2Cl\cdot BiCl_3$ and $(RN_2Cl)_3\cdot BiCl_3$. Also, with the *p*-tolyl radical, the complex always was of the $(RN_2Cl)_3\cdot BiCl_3$ type; and with the *o*-tolyl radical apparently of the $RN_2Cl\cdot BiCl_3$ type, regardless of the ratio of the reactants. Ammerlahn[2c] reported that the amount of free acid available during the course of the reaction affects the ratio in the complex, but this has not been confirmed in our work.

Our particular interest in the constitution of the complexes is based on the observation by Nesmeyanov that complexes of the general formula $(RN_2Cl)_2\cdot HgCl_2$ were less suitable than $RN_2Cl\cdot HgCl_2$ types for conversion to organomercury compounds. Inasmuch as the diazonium method has proved so very successful with organomercury compounds, it was expedient to determine the type of bismuth complex most suitable for conversion to organobismuth compounds. Of the ten complexes successfully converted to organobismuth compounds, eight had the structure $(RN_2Cl)_2\cdot BiCl_3$. However, the other two complexes, $o\text{-}CH_3C_6H_4N_2Cl\cdot BiCl_3$ and $(p\text{-}CH_3C_6H_4N_2Cl)_3\cdot BiCl_3$, also gave comparatively good yields of the corresponding R_3Bi compounds. It would appear, therefore, that the composition of the complex has no significant effect on the eventual formation of the organobismuth compound.

Intermediate Compounds.—When the *o*-carbomethoxybenzenediazonium chloride–bismuth

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(1) Bart, *Ann.*, **429**, 55 (1922); German pat. 250,264, Aug. 1, 1910 [*Chem. Zentr.*, **83**, II, 882 (1912)].

(2) (a) Challenger and Wilkinson, *J. Chem. Soc.*, **121**, 91 (1922); (b) Supniewski and Adams, THIS JOURNAL, **48**, 507 (1926); (c) Günther Ammerlahn, Ph.D. Dissertation, Friedrich-Wilhelms University, Berlin, 1927.

(3) Gilman and Svigoon, THIS JOURNAL, **61**, 3586 (1939).

(4) Nesmeyanov, Kocheshkov and Klimova, *Ber.*, **68**, 1877 (1935); Kocheshkov and Nesmeyanov, *J. Gen. Chem.* (U. S. S. R.), **6**, 144 (1936).

(5) Charrier, *Atti accad. Lincei*, [6] **5**, 889 (1927).

chloride complex in absolute ethanol was treated with four equivalents of copper bronze, two organobismuth chlorides were formed: *o*-carbomethoxyphenylbismuth dichloride, *o*-$CH_3O_2CC_6H_4BiCl_2$, and di-*o*-carbomethoxyphenylbismuth chloride, $(o\text{-}CH_3O_2CC_6H_4)_2BiCl$. From a corresponding reaction with the *o*-carboethoxybenzenediazonium chloride complex there was obtained di-*o*-carboethoxyphenylbismuth chloride. Also, diphenylbismuth chloride has been isolated from the copper bronze decomposition of the benzenediazonium complex. Accordingly, the reaction proceeds by way of an intermediate organobismuth chloride, and is essentially similar to the corresponding reactions whereby organomercury,[6a] organolead[6b] and organotin[6b] compounds are produced. In these three cases, the respective intermediates are RHgX, R_2PbX_2, R_3PbX and R_2SnX_2.

Conversion of Organobismuth Chloride Intermediates to R_3Bi Compounds.—We have shown that the copper bronze treatment of the diazonium chloride–bismuth chloride complexes does not yield R_3Bi compounds directly. In the first report,[3] we described the use of ammonium hydroxide in conjunction with copper to convert the diazonium complex to R_3Bi compound. Copper and ammonium hydroxide[6a] and copper and pyridine[7] have been used for the conversion of RHgX to R_2Hg. However, it has been shown that hydrazine hydrate is a reagent of choice for converting RHgX to R_2Hg compounds,[8a] and R_2BiX and $RBiX_2$ to R_3Bi compounds.[8b] Actually, our optimal yields of R_3Bi compounds were obtained when the diazonium complex was treated successively with copper bronze and hydrazine. In some instances, such as with di-*o*-carbomethoxyphenyl bismuth chloride, hydrazine cannot be used probably because of secondary reactions.

Other procedures have been examined for the conversion of the diazonium complexes to the corresponding organobismuth compounds. Waters[9a,b,c] has shown that the decomposition of aryldiazonium chlorides by bismuth metal cannot be used to prepare organobismuth compounds, under conditions where mercury, antimony, arsenic and tin will react to form the corresponding organometallic compounds. We have shown that the decomposition of a diazonium chloride–zinc chloride complex or a diazonium fluoride–boron fluoride complex, in the presence of bismuth chloride, by copper bronze or cuprous chloride, does not yield organobismuth compounds. This also is in contrast with the preparation of other organometallic compounds, for it has been shown[10] that organomercury and organoarsenic compounds can be obtained by the decomposition of boron fluoride complexes by cuprous chloride in the presence of mercuric chloride and arsenic chloride, respectively. Organoantimony compounds have been prepared by the decomposition of diazonium chloride–zinc chloride complexes by antimony.[9b]

Inasmuch as the decomposition of aryldiazonium chlorides in organic solvents may lead to the formation of hydrogen chloride, calcium carbonate was used[9a] to maintain neutral conditions. Possible secondary cleavage reactions by acid were ruled out in our work because the yields of R_3Bi compound were identical in the presence or absence of calcium carbonate.

Secondary Reactions.—The decomposition of the diazonium complexes may lead to the reactions

$$(C_6H_5N_2Cl)_2\cdot BiCl_3 + 4Cu \longrightarrow (C_6H_5)_2BiCl + 4CuCl + 2N_2 \qquad [1]$$

$$(C_6H_5N_2Cl)_2\cdot BiCl_3 \xrightarrow{[Cu]} 2C_6H_5Cl + 2N_2 + BiCl_3 \qquad [II]$$

$$(C_6H_5N_2Cl)_2\cdot BiCl_3 \xrightarrow{[Cu]} C_6H_5N_2Cl + C_6H_6 \longrightarrow C_6H_5N{=}NC_6H_5 \qquad [III]$$

$$(C_6H_5N_2Cl)_2\cdot BiCl_3 + 2Cu \longrightarrow C_6H_5\cdot C_6H_5 + 2CuCl + 2N_2 + BiCl_3 \qquad [IV]$$

$$(C_6H_5N_2Cl)_2\cdot BiCl_3 + 2Cu \longrightarrow 2C_6H_6 + 2CuCl + 2N_2 + BiCl_3 \qquad [V]$$

The most serious secondary reactions are [II] and [III] which result in the formation of aryl chlorides and azo compounds, respectively. Additional studies may reveal experimental conditions which will more highly subordinate the side-reactions. There may be inherent limitations in regulating the several competitive reactions. For example, although the copper bronze decomposition of aryldiazonium chloride–mercuric chloride complexes gives RHgX compounds

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(6) (a) Nesmeyanov and co-workers, *Ber.*, **62**, 1010, 1018 (1929); **67**, 130, 971 (1934); *J. Gen. Chem.* (U. S. S. R.), **1**, 598, 1162 (1931); **4**, 664 (1934); "Organic Syntheses," **12**, 46, 54 (1932); *Uspekhi Khim.* (U. S. S. R.), **3**, 34 (1934) [*C. A.*, **29**, 1075 (1935)]; (b) Nesmeyanov and co-workers, *Ber.*, **68**, 1877 (1935); *J. Gen. Chem.* (U. S. S. R.), **6**, 167, 172 (1936); *Uchenuie Zapiski* (*Wiss. Ber. Moskau Staats-Univ.*), **3**, 291 (1934) [*Chem. Zentr.*, **106**, II, 3899 (1935)].

(7) Hein and Wagler, *Ber.*, **58**, 1499 (1925).

(8) (a) Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933); Gilman and Barnett, *Rec. trav. chim.*, **55**, 563 (1936); (b) Gilman and Yablunky, THIS JOURNAL, **62**, 665 (1940).

(9) (a) Waters, *J. Chem. Soc.*, 2007 (1937); (b) 843 (1938); (c) 864 (1939).

(10) Dunker, Starkey and Jenkins, THIS JOURNAL, **58**, 2308 (1936). See, also, Abstracts, Cincinnati Meeting, A. C. S., 1940.

in excellent yields, the corresponding reactions with tin chloride- and lead chloride–diazonium chloride complexes indicate that the yields of R_2SnX_2 and R_2PbX_2 types, respectively, are generally quite poor. With triphenylbismuth, the yield is 22%; and the yields of other organobismuth compounds reported at this time do not exceed 10.3%.

Despite the low yields, the procedure may be of value in some syntheses. For example, even though the diazonium reaction gave but a 7% yield of tri-*p*-bromophenylbismuth, the reaction between *p*-bromophenylmagnesium bromide and bismuth halide gave an even smaller yield, and the crude oily product was extremely difficult to crystallize and purify.[11] The diazonium reaction yields a crystalline product which is easily purified.

More disappointing than the low yields, were the as yet unsuccessful attempts to convert some substituted benzenediazonium complexes to the corresponding organobismuth compounds. This applies particularly to some of the compounds having water-solubilizing substituents. Somewhat related restrictions have been noted with organotin compounds, where *p*-iodobenzene- and *p*-nitrobenzenediazonium chloride–tin chloride complexes gave no organotin compounds.[12]

The following conclusions may be drawn with regard to the proposed reaction. (1) The formation of organobismuth compounds from the diazonium complexes does not take place in dry benzene, ethyl acetate or petroleum ether. (2) Organobismuth compounds do not form in absolute ethanol when powdered zinc, iron or bismuth are used as the decomposing agent. Traces of copper bronze or cuprous chloride also give negative results. However, in the same solvent, using the required amount of copper bronze and identical conditions of temperature and conversion agent (hydrazine), the formation of R_3Bi may reach 22%. (3) The formation of organobismuth compounds occurs best in absolute ethanol when copper bronze is used as the decomposing agent, at room temperature, and the heat of reaction is allowed to cause refluxing of the alcohol. At this point, conversion with hydrazine is preferable to ammonium hydroxide. (4) Although organobismuth compounds form in acetone and dry dioxane, these solvents are less satisfactory because of the greater formation of azo compounds (Reaction III) which not only reduces the yield but also makes purification of the R_3Bi compound more difficult. In addition, although these conditions are suitable for the preparation of triphenylbismuth and tri-*p*-tolylbismuth, they are not so generally applicable with other complexes as the conditions described in (3).

Organobismuth Halides.—Two special properties of organobismuth halides were observed. The *o*-carbomethoxyphenylbismuth dichloride, di-*o*-carbomethoxyphenylbismuth chloride and di-*o*-carboethoxyphenylbismuth chloride mentioned earlier have unusual stability. Although compounds of the types $RBiX_2$ and R_2BiX are very sensitive to moisture and alcohol and are not very stable even when kept dry, the three compounds mentioned are stable for months even when no precautions are taken to exclude moisture, and they may be crystallized from alcohol. Their stabilities far exceed that of diphenylbismuth chloride or phenylbismuth dichloride.

Incidental to an examination of the mechanism of formation of triphenylbismuth from the diazonium complex, sodium iodide was added to convert any intermediately formed diphenylbismuth chloride to the more stable diphenylbismuth iodide. The reaction did not go in the expected manner, for iodine was liberated and the product isolated was triphenylbismuth. Under similar conditions, no tri-*p*-tolylbismuth or tri-*p*-bromophenylbismuth was formed when the corresponding complexes were treated with sodium iodide.[13a] The formation of triphenylbismuth subsequent to the sodium iodide treatment is highly anomalous since we showed recently[14] that pure diphenylbismuth chloride and sodium iodide in absolute ethanol give diphenylbismuth iodide in excellent yields. The abnormal reaction is very probably due to the presence of compounds other than diphenylbismuth chloride which react with the sodium iodide.[13b] In support of such an interpretation, we found that if the reaction mixture obtained by decomposition of the diazonium complex is centrifuged, and the clear supernatant ethanolic solution treated with sodium iodide, no iodine is liberated and diphenylbismuth iodide but no triphenylbismuth is formed.

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[11] Challenger and Ridgway, *J. Chem. Soc.*, **121**, 104 (1922); our own experience confirms this entirely.

[12] Kocheshkov, Nesmeyanov and Klimova, *J. Gen. Chem.* (U. S. S. R.), **6**, 172 (1936).

[13] (a) Sodium iodide has been used to convert RHgX to R_2Hg. (b) The possibility of secondary catalytic reactions is not ruled out.

[14] Gilman and Yablunky, THIS JOURNAL, **63**, 207 (1941).

Experimental Part

Analysis for Bismuth.—A modification of the procedure of Schoeller and Waterhouse[15] was used for the bismuth analysis. The compound (0.2–0.4 g.) was heated with 10 cc. of concd. sulfuric acid in a 400 cc. beaker covered with a watch glass. When sulfur trioxide fumes evolved, the beaker was removed from the source of heat and allowed to cool. Then 5 cc. of concd. nitric acid was added and heating to the evolution of sulfur trioxide repeated. If the cooled liquid was colorless or pale yellow, the oxidation was considered complete; if, however, the liquid was dark in color, the nitric acid treatment was repeated. The cooled contents in the beaker were then diluted with 25 cc. of distilled water; made just alkaline with ammonia (1:1); then just acid with 1 cc. of concd. nitric acid; and heated until the bismuth hydroxide dissolved completely. At this acidity, the hydroxide does not dissolve readily. To the clear solution, at the boiling point, was added dropwise and with stirring a 10% solution of diammonium hydrogen phosphate. The following data give the number of cc. of the reagent required for complete precipitation of the bismuth.

cc. $(NH_4)_2HPO_4$	g. Bi available in sample
30; 40; 50	0.10; 0.20; 0.30

The contents of the beaker were then diluted to 400 cc. with hot water, allowed to digest for one hour, filtered through a weighed Gooch crucible, the $BiPO_4$ washed with 3% ammonium nitrate solution, dried at 100°, placed within another crucible, and ignited at a pale red heat to constant weight.

Preparation of Diazonium Chloride–Bismuth Chloride Complexes. Procedure I.—One-tenth mole of the amine was dissolved in 100 cc. of hydrochloric acid (1:1), by heating where necessary. Rapid cooling by means of an ice-bath precipitated the amine hydrochloride in finely divided form. The rapidly stirred suspension was diazotized with 7 g. of sodium nitrite dissolved in a minimum of water. The diazonium solution was filtered rapidly through a Büchner funnel using suction, and to the clear filtrate was added with stirring, the theoretical amount of bismuth chloride in iced hydrochloric acid solution (0.05 mole bismuth chloride per 20 cc. concd. HCl). After stirring for an additional ten minutes, the precipitated complex was filtered; washed with ice-cold methanol and then with a little anhydrous ether, and air-dried. Prior to use in a reaction, the diazonium complex was dried in a vacuum desiccator over sulfuric acid. If no complex precipitated because of water-solubility, precipitation was effected by the addition of 100 cc. of ice-cold methanol. Our present experience is that ethanol or higher alcohols are not more effective than methanol.

Procedure II.—To the ice-cold solution of 0.1 mole of the amine in 50 cc. of ether was added, with vigorous stirring, a solution made by mixing 11.4 g. (0.165 mole) of sodium nitrite dissolved in a minimum of water and 0.05 mole of bismuth chloride in 50 cc. of concd. hydrochloric acid, at −10°. After stirring for fifteen minutes, the diazonium complex was filtered, washed as in Procedure I, and air-dried.

The complexes could not be purified readily and the analyses for bismuth were run directly on the crude, desiccator-dried compound. Agreement between the theoretical and the calculated values was generally rather good but indicated that the complexes were slightly impure. The formula, procedure, per cent. yield, and decomposition temperature of the complexes prepared are: $(C_6H_5N_2Cl)_2\cdot BiCl_3$, I (88), II (100), 94°; $o\text{-}CH_3C_6H_4N_2Cl\cdot BiCl_3$, I (75.8), 82°; $(p\text{-}CH_3C_6H_4N_2Cl)_3\cdot BiCl_3$, I (75.1), II (100), 127° (fuses at 110°); $(\alpha\text{-}C_{10}H_7N_2Cl)_2\cdot BiCl_3$, I (61.5), 120°; $(\beta\text{-}C_{10}H_7N_2Cl)_2\cdot BiCl_3$, I (70.3) 118°; $(o\text{-}ClC_6H_4N_2Cl)_2\cdot BiCl_3$, I (77.2) 160°; $(p\text{-}ClC_6H_4N_2Cl)_2\cdot BiCl_3$, I (71.5), II (84.8), 154°; $(o\text{-}BrC_6H_4N_2Cl)_2\cdot BiCl_3$, II (94), 155°; $(p\text{-}BrC_6H_4N_2Cl)_2\cdot BiCl_3$, I (87.3), II (98.6), 147° (fuses at 120°); $(p\text{-}IC_6H_4N_2Cl)_2\cdot BiCl_3$, I (71.8), 129°; $(o\text{-}CH_3OC_6H_4N_2Cl)_2\cdot BiCl_3$, I (54.8), 153°; $(p\text{-}CH_3OC_6H_4N_2Cl)_2\cdot BiCl_3$, I (45.7), 145°; $(o\text{-}CH_3O_2CC_6H_4N_2Cl)_2\cdot BiCl_3$, I (67), II (90), 122°; $(o\text{-}C_2H_5O_2CC_6H_4N_2Cl)_2\cdot BiCl_3$, I (81), 115°; $(p\text{-}C_2H_5O_2CC_6H_4N_2Cl)_2\cdot BiCl_3$, I (73.5), 91° (complex decompd. spontaneously); $(p\text{-}H_2NSO_2C_6H_4N_2Cl)_2\cdot BiCl_3$, I (96.4), 123°; $(p\text{-}C_6H_5C_6H_4N_2Cl)_3\cdot BiCl_3$, 121°.

Procedures I and II were not applicable in the preparation of the following two complexes and these are described separately, as is also the case with some complexes other than those of the diazonium chloride–bismuth chloride type.

***p*-Carboxybenzenediazonium Chloride–Bismuth Chloride Complex.**—Thirteen and seven-tenths grams (0.1 mole) of *p*-aminobenzoic acid, 14.3 g. of anhydrous sodium carbonate, and 8.0 g. of sodium nitrite were dissolved in 200 cc. of water and the solution heated to boiling. After cooling to 0°, the solution was added slowly and with stirring to 100 cc. of concd. hydrochloric acid and 100 g. of ice. After five minutes, 15.8 g. (0.05 mole) of bismuth chloride in 15 cc. of concd. hydrochloric acid was added. The complex which precipitated weighed 16.8 g. (58.5% yield) after filtering and drying. It decomposes at 103°.

***p*-Sulfobenzenediazonium Chloride–Bismuth Chloride Complex.**—To a rapidly stirred ice-cold suspension of 2.8 g. of anhydrous sodium carbonate, 7.6 g. (0.044 mole) of finely ground sulfanilic acid and 4.0 g. (0.45 mole) of sodium nitrite in 50 cc. of water was added slowly 4 cc. of concd. hydrochloric acid. The solution was filtered and treated with 6.93 g. (0.022 mole) of bismuth chloride in 10 cc. of hydrochloric acid (1:1). The complex, which precipitated at once, was filtered, washed with alcohol, and air-dried to yield 9.67 g. (57.5%). It decomposes at 140°.

Conversion of Diazonium–Bismuth Chloride Complexes to R_3Bi Compounds.—A typical preparation is that of tri-*p*-bromophenylbismuth. A mixture of 34.8 g. (0.046 mole) of the *p*-bromobenzenediazonium chloride–bismuth chloride complex and 11.75 g. of copper bronze was treated with 100 cc. of absolute ethanol with very rapid stirring. Reaction set in instantly; the copper became dark in color; and the alcohol refluxed. After spontaneous cooling to room temperature, 10.0 g. of hydrazine hydrate was added; the reaction mixture was stirred for five hours, then poured into 500 cc. of water, and filtered. The insoluble material was dried and extracted with chloroform. The chloroform was evaporated, and then steam distillation of the residual solid yielded 4.08 g. of *p*-bromochlorobenzene. The residue remaining after the steam distillation was crystallized twice from chloroform ethanol to

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(15) Schoeller and Waterhouse, *Analyst*, **45**, 435 (1920).

yield 1.44 g. (7%) of tri-*p*-bromophenylbismuth melting at 144.5–145°.

Anal. Calcd. for $C_{18}H_{12}Br_3Bi$: Bi, 30.92. Found: Bi, 30.90.

The yields of the other triarylbismuth compounds prepared in essential accordance with the directions just given for tri-*p*-bromophenylbismuth are: triphenylbismuth (22%); tri-*o*-tolylbismuth (6.4%); tri-*p*-tolylbismuth (6.7%); tri-α-naphthylbismuth (trace); tri-*p*-chlorophenylbismuth (8.4%); tri-*o*-methoxyphenylbismuth (6.4%); and tri-*p*-methoxyphenylbismuth (1.0%).

Di-*o*-carbomethoxyphenylbismuth Chloride and *o*-Carbomethoxyphenylbismuth Dichloride.—To a stirred suspension of 59 g. (0.083 mole) of the diazonium complex in 200 cc. of absolute ethanol was added 21.6 g. of copper bronze. A vigorous reaction occurred and external cooling was required. Stirring was continued for four and one-half hours, after which the reaction mixture was poured into 500 cc. of hot water, and filtered. The insoluble material, after drying, was thoroughly extracted with chloroform and the chloroform removed by distillation to yield 6.18 g. of a tan colored solid, melting at 165°. This solid was extracted with 15 cc. of chloroform and filtered from the more insoluble material (A). The chloroform filtrate was diluted with 15 cc. of warm methanol, and on cooling there formed small colorless crystals of di-*o*-carbomethoxyphenylbismuth chloride, melting at 180–181°, in a yield of 4.37 g. (10.3%). This compound is very soluble in chloroform and dioxane; insoluble in methanol; and reacts with concd. sulfuric acid to liberate hydrogen chloride.

Anal. Calcd. for $C_{16}H_{14}O_4ClBi$: Bi, 40.66; Cl, 6.89. Found: Bi, 40.43; Cl, 7.3.

The more insoluble fraction (A) was crystallized from a large volume of chloroform to yield 0.67 g. (1.95%) of *o*-carbomethoxyphenylbismuth dichloride as faintly pink tinted crystals, melting at 220–221°, and evolving hydrogen chloride when treated with concd. sulfuric acid.

Anal. Calcd. for $C_8H_7O_2BiCl_2$: Bi, 50.36; Cl, 17.11. Found: Bi, 50.34; Cl, 17.72.

In an attempted conversion to the R_3Bi compound, 0.5 g. of di-*o*-carbomethoxyphenylbismuth chloride suspended in 15 cc. of 95% ethanol was treated with 0.2 g. of hydrazine hydrate. A reaction occurred, and the crystalline solid was replaced by a milky suspension. After stirring four and one-half hours, the mixture was poured into water and the white solid isolated by filtration weighed 0.35 g., was insoluble in organic solvents and alkali and did not melt but burned in an open flame leaving a residue of bismuth oxide. The chlorine in di-*o*-carbomethoxyphenylbismuth chloride is relatively unreactive, for no reaction took place with sodium iodide in ethanol, under conditions generally applicable for the conversion of R_2BiCl to R_2BiI. No reaction took place in the cold with the R_2BiCl compound and 10% potassium hydroxide; however, when the alkaline suspension was refluxed for one-half hour, there resulted an insoluble non-melting product which burned leaving a residue of bismuth oxide. The alkaline filtrate gave no precipitate on acidification.

Di-*o*-carboethoxyphenylbismuth Chloride.—When 29 g. (0.039 mole) of the diazonium complex in 100 cc. of absolute ethanol was treated with 10.3 g. of copper bronze, a vigorous reaction occurred after about one-half minute. The mixture was stirred for one and one-half hours, allowed to stand overnight and then poured into 400 cc. of water to give an insoluble material which was extracted with chloroform. Removal of the chloroform gave 1.37 g. of a colorless product melting at 145°. Recrystallization from chloroform–methanol (1:2) gave 1.22 g. (6.5%) of small crystals melting at 147–148°; readily soluble in chloroform and dioxane; moderately soluble in ethanol and propylene glycol; and insoluble in methanol.

Anal. Calcd. for $C_{18}H_{18}O_4ClBi$: Bi, 38.53; Cl, 6.54. Found: Bi, 38.67; Cl, 6.94.

No *o*-carboethoxyphenylbismuth dichloride was isolated.

Reactions of Benzenediazonium Chloride–Bismuth Chloride Complex.—After the initial reaction between 21.6 g. (0.036 mole) of the diazonium complex and 9.15 g. of copper bronze in 100 cc. of absolute ethanol had subsided, the mixture was centrifuged to give a clear supernatant solution (A). The residual solid material was stirred vigorously with 100 cc. of dry ether, allowed to settle and then the ether decanted (Solution B).

To the solid remaining was added 50 cc. of absolute ethanol and 10 g. of hydrazine hydrate. Stirring was continued for five hours, after which the mixture was poured into water and filtered (Solid A).

Solutions A and B were combined and distilled to remove the ether. The alcoholic solution remaining was poured into water, and the precipitated solid was filtered, dried and extracted with benzene. Evaporation of the benzene yielded 0.3 g. of diphenylbismuth chloride, melting at 180°, and further identified by conversion with hydrazine to triphenylbismuth.

Solid A yielded a trace of triphenylbismuth, due probably to some diphenylbismuth chloride which was not extracted in Solutions A and B.

The above experiments indicate that no significant quantity of triphenylbismuth is formed directly by the decomposition of the diazonium complex unless a conversion agent like hydrazine is used.

An immediate reaction took place when 6 g. (0.01 mole) of the diazonium complex suspended in 60 cc. of absolute ethanol was treated with 2.54 g. of copper bronze. After stirring an additional five minutes, 1.5 g. (0.01 mole) of sodium iodide was added. Iodine was liberated; the solution became colorless; and the suspended material turned grey in color. After stirring for eight hours, the mixture was poured into 300 cc. of hot water; the resulting precipitate was then dried and extracted with ethyl acetate. The ethyl acetate was removed under reduced pressure; the residual solid was taken up in ether; and the ether was evaporated to yield 0.52 g. (17.9%) of pure triphenylbismuth. However, if after the decomposition of the diazonium complex by copper bronze, the reaction mixture is centrifuged and the clear supernatant liquid treated with sodium iodide, a yellow precipitate forms. After stirring for four hours, this mixture was poured into water to yield a solid which was extracted with ethyl acetate. Removal of the ethyl acetate yielded 0.1 g. of diphenylbismuth iodide, but no triphenylbismuth.

The *p*-Bromobenzenediazonium Chloride–Zinc Chloride Complex.—This diazonium complex was prepared in an 82.7% yield in essential accordance with the directions of Nesmeyanov.[4] A vigorous reaction took place on the addition of a small quantity of copper bronze to 24 g. (0.042 mole) of the complex, 4.42 g. (0.014 mole) of bismuth chloride and 50 cc. of absolute ethanol. When the reaction had subsided, the mixture was cooled and treated with 5 g. of hydrazine hydrate. The yield of *p*-bromochlorobenzene was 7.5 g. (46.7%), and no tri-*p*-bromophenylbismuth was isolated.

Benzenediazonium Fluoride–Boron Fluoride Complex.—The preparation of this diazonium complex was patterned after the directions of Wilke-Dörfurt and Balz.[16] A ready reaction took place when 8.9 g. (0.05 mole) of the complex was added slowly to a stirred suspension of 5.35 g. (0.017 mole) of anhydrous bismuth chloride and 8.0 g. of copper bronze in 100 cc. of acetone. Stirring was continued until the evolution of nitrogen ceased; then, 5 g. of hydrazine hydrate was added and stirring was continued for several hours. When the reaction mixture was worked up in the usual manner, no triphenylbismuth was isolated and the highly colored product contained large quantities of azobenzene. In another reaction, the substitution of absolute ethanol for acetone also gave no triphenylbismuth.

Factors Affecting the Yields of R_3Bi Compounds from the Diazonium Complexes.—(Benzenediazonium Chloride–Bismuth Chloride Complex) (1) In methanol, 20°, copper bronze in small portions, ammonium hydroxide, yield of triphenylbismuth, 12.3%. (2) In absolute ethanol, 20°, copper bronze in small portions, sodium iodide (iodine being liberated), yield of triphenylbismuth, 17.7%. (3) As in (2) except in commercial methanol, yield of triphenylbismuth, 3.4%.

(*p*-Toluenediazonium Chloride–Bismuth Chloride Complex) (1) Acetone, 0°, copper bronze at once, ammonium hydroxide, yield of tri-*p*-tolylbismuth, 6.5%; yield of *p*-azotoluene, 25.4%. (2) As in (1), but at 20°; yield of tri-*p*-tolylbismuth, 6.5%; yield of *p*-azotoluene, 20%. (3) Acetone, 0°, complex added to suspension of copper bronze, ammonium hydroxide, yields of two products, 4.9% and 60%, respectively. (4) Methanol, 0°, copper bronze at once, ammonium hydroxide, yields, 10.8 and 25.4%, respectively. (5) Absolute ethanol, −15°, copper bronze in small portions, ammonium hydroxide, yield of tri-*p*-tolylbismuth, 14.6%; bi-*p*-tolyl, 2.8%; *p*-azotoluene, 5.2%. (6) Dry dioxane, 10°, copper bronze in small portions, ammonium hydroxide, yield of tri-*p*-tolylbismuth, 5%; bi-*p*-tolyl, 5%; *p*-azotoluene, 15%. (7) Ethyl acetate, 0°, copper bronze at once, ammonium hydroxide, no bismuth compound was obtained. The other products were not examined. (8) No bismuth compound was obtained when the conditions were absolute ethanol, 20°, copper bronze in small portions and sodium iodide (iodine being liberated).

(*p*-Bromobenzenediazonium Chloride–Bismuth Chloride Complex) (1) Acetone, 0°, copper bronze at once, ammonium hydroxide, no bismuth compound; 15% *p*-bromochlorobenzene and some azo compound. (2) Methanol, 20°, copper bronze at once, ammonium hydroxide, no bismuth compound; 2.4% azo compound. (3) Absolute ethanol, 20°, zinc dust, hydrazine, no bismuth compound; 39% bromobenzene. (4) Absolute ethanol, 20°, calcium carbonate, copper bronze at once, hydrazine; 6.7% tri-*p*-bromophenylbismuth; other products not determined. (5) Absolute ethanol, 20°, cuprous chloride, hydrazine, no bismuth compound; 28% *p*-bromochlorobenzene. (6) Absolute ethanol, 20°, iron powder, hydrazine; no bismuth compound; 48.7% *p*-bromochlorobenzene; 4.0% bromobenzene.

In the following series of experiments no tri-*p*-bromophenylbismuth was isolated, and no examination was made of the other products. (7) Absolute ethanol, 20°, copper bronze in small portions, and sodium iodide (iodine being liberated). (8) Dry benzene, 50°, copper bronze, hydrazine. (9) Dry petroleum ether, 70°, copper bronze, hydrazine. (10) Technical ethyl acetate, 20°, copper bronze, hydrazine. (11) Absolute ethanol, 20°, trace of copper bronze, hydrazine. (12) Dry ethyl acetate, 20°, copper bronze, hydrazine.

Summary

A variety of organobismuth compounds can now be prepared by means of the diazo reaction. The aryldiazonium chloride–bismuth chloride complexes are first decomposed by copper bronze to R_2BiCl and $RBiCl_2$ types. These organobismuth chlorides are then converted by hydrazine to R_3Bi types.

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[16] Wilke-Dörfurt and Balz, *Ber.*, **60**, 115 (1927).