minutes a solution of 9.0 g. (0.076 mole) of thionyl chloride in 25 cc. of ether. The rate of addition was such as to cause the ether to reflux. When about two-thirds of the thionyl chloride had been added considerable white precipitate had formed and a bath was placed under the flask to keep the ether refluxing. Stirring and refluxing were continued for three hours more at which time the mixture had developed a deep brown color. The dark red supernatant liquid was then poured off and the residue extracted with four 25-cc. portions of ether. The ethereal solutions were combined, washed with several 50-cc. portions of water and small quantities of a saturated sodium bicarbonate solution until free of acid. The neutral ether solution was then dried over anhydrous magnesium sulfate and distilled.[6] There was obtained 5.1 g. (60.7% of the theoretical) of 2-α-furylethyl chloride, b. p. 70–71° at 42 mm., 63° at 26 mm., n^{25}_D 1.4788, d^{25}_4 1.1229, MR_D (calcd.) 33.28, MR_D (obsd.) 32.95.

Anal. Calcd. for C_6H_7OCl: C, 55.16; H, 5.41. Found: C, 55.27; H, 5.91.

2-α-Furylethylmagnesium Chloride and 3-α-Furylpropionic Acid.—In a 200-cc. 3-necked flask equipped with a mercury sealed stirrer, dropping funnel and reflux condenser was placed 30 cc. of dry ether, 0.6 g. (0.025 g. atom) of magnesium and 3 g. (0.023 mole) of α-furylethyl chloride. A small crystal of iodine was added and the mixture stirred and refluxed for several hours. At the end of this time a faint turbidity was apparent but the Gilman test for a Grignard reagent[7] was negative. After about twelve hours of standing, however, much magnesium had gone into solution and the reaction was completed by refluxing and stirring for several hours more. Gilman's test was then positive. The mixture was poured onto about 100 g. of crushed dry-ice in a beaker. On working up the product in the usual way there was obtained 0.8 g. (25%) of 3-α-furylpropionic acid, which, on recrystallization from ligroin, melted at 56.6–57.6°; reported,[3] 56.5–58°.

Anal. Calcd. for $C_7H_8O_3$: C, 59.97; H, 5.75. Found: C, 59.94; H, 6.05.

Summary

1. It has been shown that ethyl-2-furanacetate may be reduced by the method of Bouveault and Blanc to 2-α-furylethanol.

2. A procedure has been developed which gives improved yields of chlorides from such alcohols as 2-α-furylethanol and 3-α-furylpropanol.

3. It has been found that 2-α-furylethyl chloride, in contrast to its adjacent compounds in the homologous series, reacts with magnesium to yield a stable and synthetically valuable Grignard reagent.

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[6] Gilman and Hewlett, ref. 3, reported a yield of 20% of 3-α-furylpropyl chloride from the alcohol. The modification of Kirner's method given here consistently yields over 40% of the same chloride.

[7] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

BETHLEHEM, PENNA. RECEIVED JUNE 29, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Unsymmetrical Organobismuth Compounds

BY HENRY GILMAN AND H. L. YABLUNKY

The only unsymmetrical organobismuth compound which has been described in any detail is diphenyl-α-naphthylbismuth, which was prepared by Challenger and co-workers.[1]

$$(C_6H_5)_2BiBr + \alpha\text{-}C_{10}H_7MgBr \longrightarrow (C_6H_5)_2BiC_{10}H_7\text{-}\alpha + MgBr_2 \quad (1)$$

Incidental to studies concerned with optically active organobismuth compounds, these authors tried unsuccessfully to prepare other unsymmetrical organobismuth compounds. More recently, Norvick[2] reported the formation of diethylamylbismuth, together with triethylbismuth and triamylbismuth, from the reaction between amylbismuth dichloride and ethylmagnesium bromide, but has not yet provided physical data on the unsymmetrical compound.

On the basis of general observations concerned with the relative reactivities of organometallic compounds,[3] it appeared quite probable that a variety of unsymmetrical compounds could be made and would be found to be reasonably stable. This has been shown to be the case. Several procedures have been used, and these are illustrated in the following reactions for the synthesis of di-*p*-tolyl-α-naphthylbismuth.

$$(p\text{-}CH_3C_6H_4)_2BiX + \alpha\text{-}C_{10}H_7MgBr \longrightarrow (p\text{-}CH_3C_6H_4)_2BiC_{10}H_7\text{-}\alpha + MgXBr \quad (2)$$

$$2p\text{-}CH_3C_6H_4MgBr + \alpha\text{-}C_{10}H_7BiBr_2 \longrightarrow (p\text{-}CH_3C_6H_4)_2BiC_{10}H_7\text{-}\alpha + 2MgBr_2 \quad (3)$$

$$(p\text{-}CH_3C_6H_4)_2BiNa + \alpha\text{-}C_{10}H_7I \longrightarrow (p\text{-}CH_3C_6H_4)_2BiC_{10}H_7\text{-}\alpha + NaI \quad (4)$$

Acting on the observation of Challenger and

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[1] (a) Challenger, *Proc. Chem. Soc.*, **29**, 76 (1913); *J. Chem. Soc.*, **105**, 2210 (1914). (b) Challenger and Allpress, *Proc. Chem. Soc.*, **30**, 293 (1914); *J. Chem. Soc.*, **107**, 16 (1915). (c) Challenger, *ibid.*, **109**, 250 (1916). (d) Challenger and Goddard, *ibid.*, **117**, 762 (1920). (e) Challenger and Allpress, *ibid.*, **119**, 913 (1921). (f) Challenger and Ridgway, *ibid.*, **121**, 104 (1922).

[2] Norvick, *Nature*, **135**, 1038 (1935).

[3] Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 482.

Allpress[1e] that the yield of their diphenyl-α-naphthylbismuth was improved by carrying out Reaction 1 at room temperature rather than at reflux temperature,[4] we found that their 16.4% yield could be increased to 57% by operating at 0°, as one of a few improvisations. Reaction IV is a liquid ammonia reaction which is described in the following paper. In the early stages of our study on Reactions 2 and 3 it appeared that one of the R groups in the unsymmetrical triarylbismuth compounds had to be the α-naphthyl radical. Subsequently it was found that the reactions were of wider scope. However, there appear to be some limitations to the types that can be formed in appreciable quantities, particularly those having radicals associated with steric influences, and studies on such types are described in the Experimental Part.

Indirect procedures were required to isolate some of the unsymmetrical compounds as solids. One of these involved the conversion of the oily $R_2R'Bi$ compound to the corresponding dichloride which was more readily purified, and then reduced by the recently described hydrazine procedure[5a] to the crystalline unsymmetrical compound.

$$R_2R'Bi \xrightarrow{[Cl_2]} R_2R'BiCl_2 \xrightarrow{[N_2H_4]} R_2R'Bi$$

In Reactions 2 and 3, the Grignard reagent and the organobismuth halide were prepared just before they were used. This is particularly important with the latter compounds. Reactions with old preparations almost invariably yielded unresolvable oils.[5b]

Stability.—Once obtained in a pure condition, the unsymmetrical compounds have a distinctly higher stability than might have been expected. For example, a sample of diphenyl-α-naphthylbismuth has been kept in a stoppered bottle for three years without alteration in melting point. In this connection it is interesting to recall the observations of Calingaert and co-workers[6] that the reputedly unstable, unsymmetrical methylethylmercury is in reality quite stable and can be distilled without undergoing disproportionation provided that traces of RHgX or other related catalysts are absent.

Redistribution Reaction.—Challenger and Ridgway[1f] also prepared diphenyl-α-naphthylbismuth by heating diphenylmercury and tri-α-naphthylbismuth at 200°, and by heating triphenylbismuth and tri-α-naphthylbismuth at 190°. In connection with their studies on the "redistribution reaction," Calingaert and co-workers[6] have suggested that a precise analysis of the Challenger reaction between triphenylbismuth and tri-α-naphthylbismuth would probably have revealed some of the other unsymmetrical product: phenyldi-α-naphthylbismuth. If this latter compound were formed it is quite understandable how it might not have been isolated, because our study of a related reaction indicates that phenyldi-α-naphthylbismuth would be difficult to separate from tri-α-naphthylbismuth because of their very closely related solubilities.

The general problem of redistribution or disproportionation of radicals is closely related to other reactions leading to the synthesis of the unsymmetrical organobismuth compounds. Challenger and co-workers[1] found that with the single exception of Reaction 1, reactions between R_2BiX and $R'MgX$ compounds always yielded R_3Bi compounds. This indicated to them the possibility that an R_2BiX compound was in reality a double salt[7] of R_3Bi and BiX_3; and that the use of a sufficient excess of $R'MgX$ should yield two symmetrical organobismuth compounds.

$$\left.\begin{array}{l} R_3Bi \\ BiX_3 \end{array}\right\rangle \xrightarrow{[3R'MgX]} R_3Bi + R'_3Bi + 3MgX_2$$

Although this did not occur when R and R′ were aryl radicals (since only R_3Bi was isolated), when R′ was an alkyl radical the odor of an alkylbismuth compound was evident. We are of the opinion that although organometallic salts in general show the following equilibria

$$R_2MX \rightleftarrows RMX_2 \leftrightarrows R_3M + MX_3$$

some of the unsymmetrical $R_2R'Bi$ compound was formed initially and then may have undergone redistribution, in part or in whole, to R_3Bi and R'_3Bi to account for the formation of any trialkylbismuth compound.

Organobismuth Halides.—Incidental to the preparation of some of the necessary intermediate organobismuth halides, we observed that tri-*o*-tolylbismuth is like tri-α-naphthylbismuth[1e] in its reaction with bismuth bromide: essentially

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[4] The low temperature technique was used with success by Kharasch and Marker, THIS JOURNAL, **48**, 3130 (1926), in the preparation of unsymmetrical organomercury compounds.

(5) (a) Gilman and Yablunky, *ibid.*, **62**, 665 (1940). (b) See Grüttner and Krause, *Ber.*, **50**, 202 (1917), for a related experience with organolead compounds.

[6] Calingaert, Soroos and Hnizda, THIS JOURNAL, **62**, 1107 (1940).

[7] Compounds of the type $R_3Bi\cdot HgCl_2$ are known: Stilp, Ph.D. Dissertation, University of Rostock, 1910.

irrespective of the quantity of bismuth bromide used in reaction with tri-*o*-tolylbismuth, the product is *o*-tolylbismuth dibromide and not di-*o*-tolylbismuth bromide. The procedure of Blicke and co-workers[8] for conversion of an organobismuth chloride to the corresponding iodide by means of sodium iodide is distinctly preferable to the reaction[1f]: $R_3Bi + I_2 \longrightarrow R_2BiI + RI$. For example, direct cleavage of tri-*p*-chlorophenylbismuth by iodine gave very poor yields of di-*p*-chlorophenylbismuth iodide in contrast to the satisfactory yields by the reaction: $R_2BiCl + NaI \longrightarrow R_2BiI + NaCl$. The yields of some known organobismuth compounds, previously unreported, are given in the Experimental Part.

Recently, Zhitkova and co-workers[10] have reported that trimesitylbismuth dibromide does not melt below 250°. This is entirely unexpected in view of the generalization[1f] that practically all triarylbismuth dibromides melt at about 100–115°. Only in the case of tri-*p*-cumylbismuth dibromide does the melting point go as high as 150°.[9] Although our melting point of trimesitylbismuth agrees with that reported,[10] we have observed that the product obtained from it and bromine melts at 91–93° and decomposes spontaneously.[11]

Tri-*p*-dimethylaminophenylbismuth.—Of the new symmetrical triarylbismuth compounds reported at this time, the most interesting one is tri-*p*-dimethylaminophenylbismuth. This is probably the first organobismuth compound reported having amino groups. When pure, the compound is reasonably stable. As might have been expected on the basis of the ready cleavage of a *p*-dimethylaminophenyl radical attached to a metal,[12] the compound was cleaved by chlorine even at 0°, incidental to an attempt to form the more stable R_3BiCl_2 type. Surprisingly enough, acetic acid in petroleum ether also cleaved the compound when an experiment was carried out to form a water-soluble acetate.

Experimental Part

The preparation of each unsymmetrical organobismuth compound has been checked at least twice in intervals of several months. Many of them have been prepared six times.

A few experiments are described in detail. The preparation of diphenyl-α-naphthylbismuth demonstrates the technique used in the preparation of the unsymmetrical tertiary bismuth compounds. The pentavalent dichlorides and dibromides were prepared under conditions similar to those described for di-*p*-tolyl-α-naphthylbismuth dichloride and di-*p*-tolyl-α-naphthylbismuth dibromide. The preparation and reactions of tri-*p*-dimethylaminophenylbismuth are given in detail; the other symmetrical and unsymmetrical tertiary bismuth compounds and their derivatives are listed in the accompanying Table I. A number of new $RBiX_2$ and R_2BiX compounds prepared in the course of this work are also given in this table. An unsuccessful attempt to prepare diphenyltriphenylmethylbismuth is described.

Diphenyl-α-naphthylbismuth.—A suspension of 4.0 g. (0.01 mole) of diphenylbismuth chloride in 30 cc. of ether (contained in a three-necked flask provided with stirrer, separatory funnel and a nitrogen atmosphere) was cooled to 0° by an external ice-bath. The addition of 0.01 mole of α-naphthylmagnesium bromide effected the formation of a clear yellow solution. Subsequent to stirring for several hours, the reaction mixture was hydrolyzed with iced water; then the ether layer was separated and filtered clear of suspended material. Removal of the ether under reduced pressure gave an oil, which crystallized when treated with 25 cc. of methanol and cooled. Recrystallization from 95% ethanol gave 2.8 g. (57%) of diphenyl-α-naphthylbismuth melting at 114–115°.

Di-*p*-tolyl-α-naphthylbismuth Dichloride.—Dry chlorine gas was bubbled into a dry chloroform solution of 2.72 g. of di-*p*-tolyl-α-naphthylbismuth cooled to 0° until a definite green color was formed. The chloroform was then partially evaporated and the addition of methanol gave a 95% yield of the dichloride which melted at 147° after crystallization from acetone.

Di-*p*-tolyl-α-naphthylbismuth Dibromide.—To a chloroform solution of 0.5 g. of di-*p*-tolyl-α-naphthylbismuth cooled in an ice-salt-bath was added a dilute solution of bromine in carbon tetrachloride until a slight excess of bromine was present. Partial evaporation of the solvents and the addition of methanol gave 0.59 g. (90%) of the dibromide, which after recrystallization from chloroform–methanol melted at 126–127°. The melting point varied appreciably with the rate of heating, a common phenomenon with R_3BiX_2 types.

Reaction between Diphenylbismuth Chloride and Triphenylmethylmagnesium Chloride.—A suspension of 5.76 g. (0.014 mole) of diphenylbismuth chloride in 50 cc. of ether was treated with 0.014 mole of triphenylmethylmagnesium chloride. The addition of methanol to the oil obtained in the usual manner precipitated 1.25 g. of a solid (A) melting over the range 54–60°. This colorless solid turned a deep yellow when dry. Evaporation of the methanol filtrate from A gave 3.4 g. of an orange colored solid (B). Two crystallizations of A from chloroform–methanol gave a colorless solid melting at 59–60°.

Anal. Calcd. for $(C_6H_5)_2BiC(C_6H_5)_3$: Bi, 34.48. Found: Bi, 27.63.

When B was dissolved in chloroform–ethanol, and fil-

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(8) Blicke, Oakdale and Smith, THIS JOURNAL, **53**, 1025 (1931).

(9) Gillmeister, *Ber.*, **30**, 2843 (1897).

(10) Zhitkova, Sheverdina and Kocheshkov, *J. Gen. Chem.* (U. S. S. R.), **8**, 1839 (1938).

(11) Zhitkova and co-workers have also prepared trimesitylbismuth dichloride, and report that it decomposes without melting at 150°. Our attempt to prepare the dichloride in benzene, rather than in petroleum ether as they did, led to a nuclear chlorinated dichloride which melted at 150°.

(12) Gilman, Towne and Jones, THIS JOURNAL, **55**, 4689 (1933).

TABLE I

PHYSICAL DATA AND ANALYSES OF ORGANOBISMUTH COMPOUNDS

Compound[o]	Method[a]	M. p., °C.[b]	Yield, %	Bi, %		Other, %	
				Calcd.	Found	Calcd.	Found
o-Tolylbismuth dibromide[d]		181	95.5	45.44	45.66	Br, 34.78	34.35
Di-*p*-tolyl-							
-bismuth iodide[c,p]		147–148	45.5	40.36	40.71, 40.85		
-α-naphthylbismuth	I	129–130	21.1	40.35	40.32	C, 55.7	55.6
						H, 4.07	4.07
-α-naphthylbismuth[g]	II	129–130	42.0				
-α-naphthylbismuth							
dichloride[r]		147	95.0			Cl, 12.06	12.12
dibromide[h]		126–127	90.0	30.83	30.88	Br, 23.60	24.25
-*p*-chlorophenylbismuth	I	96– 97	55.0	41.6	41.61	Cl, 7.07	7.64
Di-*o*-tolyl-α-naphthylbismuth[j]	II	112–114	59.5	40.35	39.96		
dichloride		140	59.5	35.48	35.42	Cl, 12.06	12.63
dibromide		122	76.5	30.83	30.87	Br, 23.60	24.14
Di-*p*-chlorophenyl-							
-bismuth chloride		158–160	89.3	44.7	46.2		
-bismuth iodide[e]		139–140	34.7				
-α-naphthylbismuth	I	137–138	25.3	37.40	37.18	C, 47.2	47.2
						H, 2.68	2.82
-α-naphthylbismuth	II	138–139	46.8			Cl, 12.69	13.4
-α-naphthylbismuth							
dichloride[i]		132	85.0			Cl, 22.52	22.74
dibromide		102–103	88.6	29.07	29.44		
-*o*-tolylbismuth	II	104–104.5	45.2	39.96	40.04	Cl, 13.58	13.86
dichloride		132–133	86.5	35.18	35.14		
dibromide		109–110	92.0	30.60	30.35		
Diphenyl-							
-α-naphthylbismuth[f,q]	I	114–115	57.0				
-*p*-chlorophenylbismuth[k]	I	83– 83.5	33.0	44.05	44.11	Cl, 7.48	7.65
-*p*-tolylbismuth dichloride[l]		109–110	46.8	39.82	39.98	Cl, 13.52	13.67
Di-*p*-anisyl-α-naphthylbismuth	II	135–136	10.9	38.0	37.99, 37.95		
Di-*p*-phenetyl-α-naphthylbismuth	II	131–132	13.9	36.24	36.14, 36.15		
Dimesityl-α-naphthylbismuth	II	151–151.5	31.4	36.41	36.33, 36.46		
Tri-2-*p*-cymylbismuth[q]		87	36.1	34.36	33.98, 34.12		
dichloride		163–164	89.4	30.77	30.74	Cl, 10.44	10.36
dibromide		101–103	84.0	27.15	27.24	Br, 20.81	21.49
Tri-*o*-phenetylbismuth							
dibromide[m]		127–128	100			Br, 21.83	21.20
Trimesitylbismuth		134–135	40.6	36.90	36.45, 36.66		
Tri-*p*-fluorophenylbismuth[q]		93– 94	66.1	42.31	42.35		
Tri-*o*-chlorophenylbismuth[n,r]		141	14.4	38.45	38.35		

[a] In the preparation of the unsymmetrical organobismuth compounds, $R_2R'Bi$, Method I indicates that R′ was introduced by the reaction: $R_2BiX + R'MgX \longrightarrow R_2R'Bi$. When $R'BiX_2$ and 2RMgX gave $R_2R'Bi$, the preparation is designated as Method II. [b] All melting points are uncorrected. [c] The di-*p*-tolylbismuth chloride used to prepare this compound was obtained in 93.3% yield by mixing the dry ether solutions of 9.6 g. (0.02 mole) tri-*p*-tolylbismuth and 3.15 g. (0.01 mole) bismuth chloride. The method of Blicke, Oakdale and Smith[8] was used for the preparation of di-*p*-tolylbismuth iodide. [d] After shaking an ether solution of 2.41 g. (0.005 mole) of tri-*o*-tolylbismuth and 1.12 g. (0.0025 mole) of bismuth bromide for fifteen minutes, there was obtained 1.31 g. (18%) of *o*-tolylbismuth dibromide. From the ether there was recovered 1.98 g. (82%) of unreacted tri-*o*-tolylbismuth. When the reaction was carried out with 1.64 g. (0.0033 mole) of tri-*o*-tolylbismuth and 3.0 g. (0.0067 mole) of bismuth bromide, the yield of *o*-tolylbismuth dibromide was 4.4 g. (95.5%). [e] Challenger and Ridgway[1f] mention two melting points for this compound, 113° and 139°. [f] The diphenylbismuth chloride used in this reaction was prepared in 99.4% yield by mixing ether solutions of 35 g. (0.0795 mole) of triphenylbismuth and 18.2 g. (0.0574 mole) of bismuth chloride. The corresponding iodide was obtained in 64.8% yield (8). [g] The α-naphthylbismuth dibromide was prepared by mixing solutions of 5.9 g. (0.01 mole) of tri-α-naphthylbismuth in 200 cc. of dry chloroform and 8.2 g. (0.018 mole) bismuth bromide in ether. The yield was 13.2 g. (89%). When dry benzene was substituted for the chloroform the yield was 80%. [h] The melting point varied appreciably with the rate of heating, a common phenomenon with R_3BiX_2 compounds. [i] The melting point bath was heated initially to 100°. [j] The oil obtained from a reaction between 12.0 g. (0.0242 mole) of α-naphthylbismuth dibromide and 0.0484 mole of *o*-tolylmagnesium bromide resisted crystallization and so was dissolved in dry chloroform and treated with chlorine.

Partial evaporation of chlorine followed by the addition of methanol precipitated an oil which crystallized on cooling. One crystallization from chloroform–methanol gave the pure dichloride, m. p. 140°. A suspension of di-*o*-tolyl-α-naphthylbismuth dichloride in 50 cc. of 95% ethanol was treated with 2.0 g. hydrazine hydrate.[5a] After stirring for one hour the suspension was filtered to give a quantitative yield of di-*o*-tolyl-α-naphthylbismuth. [k] The diphenylbismuth bromide used in this preparation was obtained from a reaction in ether between 2.2 g. (0.005 mole) of triphenylbismuth and 1.12 g. (0.0025 mole) of bismuth bromide. The yield was 2.2 g. (85%). [l] Diphenyl-*p*-tolylbismuth is an oil at room temperature. [m] Tri-*o*-phenetylbismuth was prepared by Gilman, Yablunky and Svigoon, THIS JOURNAL, **61**, 1170 (1939). The dibromide underwent spontaneous decomposition after standing for several days. [n] The crude product was very oily and a crystalline solid was obtained only after prolonged cooling. [o] Recrystallized from chloroform–ethanol except when stated otherwise in the footnotes. [p] Crystallized from ethyl acetate. [q] Crystallized from ethanol. [r] Crystallized from acetone.

tered from a small amount of orange colored solid and cooled, triphenylbismuth (mixed m. p.) separated.

Tri-*p*-dimethylaminophenylbismuth.—To a solution of *p*-dimethylaminophenyllithium prepared[13] from 0.4 mole of freshly distilled *p*-bromodimethylaniline and 0.8 g. atom of lithium in 500 cc. of ether was added dropwise 37.8 g. (0.12 mole) of bismuth chloride in ether. The flask was protected from strong light during and subsequent to the addition of the bismuth chloride. After stirring at room temperature for eight hours, the reaction mixture was hydrolyzed with ice water, and the insoluble material extracted with chloroform. These extracts were then concentrated under reduced pressure to about one-fourth of their original volume while being protected from light. The addition of several volumes of methanol precipitated the tri-*p*-dimethylaminophenylbismuth; 6.8 g. (9.95%); m. p. 216°. The compound was slightly impure as indicated by its faint tan color; and even in the dark decomposed to give an insoluble violet colored solid. Purification was effected by dissolving in the minimum quantity of cold chloroform, filtering, and precipitating by the slow addition of three volumes of methanol. The R_3Bi compound after these treatments was obtained as small colorless crystals, melting at 230° with prior darkening, and essentially unaffected by light. The compound is very soluble in chloroform; moderately soluble in dioxane; and insoluble in ether, alcohol, propylene glycol, peanut oil and olive oil.

Anal. Calcd. for $C_{24}H_{30}N_3Bi$: Bi, 36.71; N, 7.38. Found: Bi, 36.45 and 36.44; N, 7.25.

One gram of the R_3Bi compound was boiled with 5 cc. of concd. hydrochloric acid until complete solution occurred. After cooling, the solution was made alkaline and then filtered. From the filtrate was obtained dimethylaniline, which was identified by its picrate (m. p., 159–161°) and by comparison of the picrate with an authentic specimen.

In an attempted preparation of the triacetate of tri-*p*-dimethylaminophenylbismuth, 0.6 g. (0.001 mole) of the bismuth compound in chloroform was treated with 0.18 g. (0.003 mole) of glacial acetic acid in petroleum ether. A flocculent precipitate formed, and this was free of nitrogen and blackened on the addition of sodium stannite. Apparently cleavage to an inorganic bismuth compound occurred.

The addition of dry gaseous chlorine to a solution of one gram of the R_3Bi compound in chloroform cooled to 0° induced immediate formation of a red solid which then turned green. The green solid was insoluble in chloroform, did not melt, and burned in an open flame leaving a residue of bismuth oxide. Apparently cleavage took place, without the formation of any appreciable quantity of tri-*p*-dimethylaminophenylbismuth dichloride.

Trimesitylbismuth Dibromide.—In an attempted preparation of trimesitylbismuth dibromide by titrating a −15° chloroform solution of the R_3Bi compound with bromine, there was obtained 2.42 g. (56.5%) of yellow plates melting at 91–93° after adding methanol to the concentrated chloroform solution. When moist with solvent, this compound was stable; but when dry, it decomposed spontaneously yielding a yellow oil and liberating much heat. In one preparation, the compound was decomposing after only two minutes in a vacuum desiccator over calcium chloride, and decomposition was complete before transferral could be made to a weighing bottle.

Trimesitylbismuth and Chlorine.—One gram of trimesitylbismuth dissolved in dry benzene was treated with dry gaseous chlorine until an excess was evident. Partial evaporation of the benzene, followed by the addition of methanol, gave 0.85 g. of a pale green solid melting at 149–150°. The melting point was not changed after crystallization from a mixture of chloroform and methanol.

Anal. Calcd. for $C_{27}H_{33}Cl_2Bi$: Bi, 32.80; Cl, 11.13. Calcd. for $C_{27}H_{31}Cl_4Bi$: Bi, 29.6; Cl, 20.1. Calcd. for $C_{27}H_{30}Cl_5Bi$: Bi, 28.08; Cl, 23.85. Found: Bi, 28.15; Cl, 20.00. Apparently some nuclear chlorinated trimesitylbismuth dichloride was formed.

Summary

Reactions are described for the synthesis of a series of hitherto inaccessible unsymmetrical triarylbismuth compounds, $R_2R'Bi$. When pure, these compounds are quite stable and have no special tendency to undergo disproportionation.

Of the new symmetrical triarylbismuth compounds reported, the most interesting is the basic tri-*p*-dimethylaminophenylbismuth, $[p\text{-}(CH_3)_2NC_6H_4]_3Bi$, which is highly sensitive to cleavage reagents including acetic acid.

AMES, IOWA RECEIVED OCTOBER 4, 1940

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(13) Gilman, Zoellner and Selby, THIS JOURNAL, **55**, 1252 (1933).