

Methyl Pyrazine-carboxylate.—10.5 g. of oven-dried pyrazine-carboxylic acid in 105 g. of absolute methyl alcohol saturated with dry hydrogen chloride was distilled at reduced pressure to remove excess hydrogen chloride. The residue was neutralized with saturated sodium carbonate solution and extracted with ethyl acetate. After evaporation of the ethyl acetate the solid reddish-yellow residue was sublimed at 4 mm. in an oil-bath at 100°. The pure white crystals melted at 59° unchanged after several recrystallizations from ether and other solvents (m. p. 62°; British Patent 451,304); yield 8.4 g. or 72%.

Pyrazine-carboxylamide.—8.4 g. of methylpyrazine-carboxylate in 8.4 g. of warm methyl alcohol was added to a saturated absolute methyl alcohol (17 g., 0°) solution of ammonia. The white crystals were filtered off the next day, washed with methanol, ether and dried: m. p. 189° (lit. m. p. 188°; British Patent 451,304); yield 6.9 g. or 92%.

Aminopyrazine.—After dissolving 4.2 g. of chlorine in 13.8 g. of sodium hydroxide and 150 g. of ice and water, 6.9 g. of finely powdered pyrazine-carboxylamide was added. The solution was warmed, with stirring for one hour.

The next day, the needle-like crystals were filtered off and dried; 3.5 g. of the product dissolved in water gave an alkaline solution which evolved carbon dioxide on acidification. The ethyl acetate extract of the neutralized solution was evaporated, leaving a solid yellowish residue which sublimed completely at 3 mm.; temp. of oil-bath 100°; yield, 1.5 g. of pure aminopyrazine.

The original filtrate was acidified and an alcoholic picric acid solution added. The picrate obtained and washed with alcohol, ether and dried had no definite m. p. but decomposed at 214 to 250°. The suspension of the picrate in cooled ether was saturated with hydrogen chloride. The hydrochloride filtered off and washed with ether was

neutralized with saturated sodium carbonate solution and extracted with ethyl acetate. The residue remaining after the evaporation of the ethyl acetate was sublimed at 3 mm.; temp. of oil-bath 100°; yield of aminopyrazine, 0.9 g.; combined yields of aminopyrazine 2.9 g. or 55%; m. p. 117–118° (lit. m. p. 110–117°, Gabriel and Sonn).

Anal. Calculated for $C_6H_5N_3$: C, 50.5; H, 5.30; N, 44.2. Found: C, 50.4, 50.3; H, 5.16, 5.16; N, 44.1, 43.9.

Acetaminopyrazine.—M. p. 133°.

Anal. Calculated for $C_8H_7H_3O$: C, 52.54; H, 5.11; N, 30.66. Found: C, 52.50, 52.73; H, 6.25, 6.15; N, 28.99.

Intermediate Product in the Hofmann Reaction.—The properties of the needle-like crystals obtained were found to be as follows: no definite m. p.; began to turn brown at 257°; black at 275°; very soluble in water to give an alkaline solution; insoluble in organic solvents including absolute alcohol; contains sodium; halogen test negative; effervesces (CO_2 evolved) in dilute acid (mineral or acetic) to form aminopyrazine. The intermediate compound evidently is sodium pyrazine carbamate. *Anal.* Calculated for $C_6H_4N_3O_2Na$: N, 26.1; Na, 14.3. Found: N, 25.9; Na, 14.4.

Summary

1. The Hofmann degradation on pyrazine carboxylamide gave a 55% yield of aminopyrazine, m. p. 117–118°.

2. From the Hofmann reaction an intermediate compound was isolated and identified as sodium pyrazine-carbamate, which on acidification gave aminopyrazine and carbon dioxide.

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RECEIVED OCTOBER 25, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

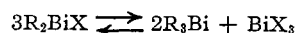
The Conversion of Arylbismuth Halides to Triarylbismuth Compounds

BY HENRY GILMAN AND H. L. YABLUNKY

We have observed that one of the intermediate types formed in the recently described synthesis of triarylbismuth compounds by the diazonium reaction¹ is R_2BiX . This suggested an examination of procedures for the conversion of such compounds to the R_3Bi compounds. The best reagent, we now find, for this purpose is hydrazine hydrate. This reagent was first used to convert 2-furylmercuric chloride and phenylmercuric chloride to 2,2'-difurylmercury and diphenylmercury, respectively²; and it was shown subsequently

that hydrazine is a reagent of choice for converting $RHgX$ to R_2Hg compounds.³

If the equilibrium



is valid, then one of the functions of the hydrazine may be to reduce the bismuth halide. The procedure was next extended successfully to the conversion of phenylbismuth dibromide to triphenylbismuth, and to the conversion of R_3BiX_2 compounds to the corresponding triarylbismuth compounds. Attention might be directed to two

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

(2) Gilman and Wright, *ibid.*, **55**, 3302 (1933).

(3) Gilman and Barnett, *Rec. trav. chim.*, **55**, 563 (1936).

interesting cases of the conversion of triarylbi-smuth dihalides to the triarylbi-smuths. First, the very stable triphenylbi-smuth difluoride is converted rapidly and practically quantitatively to triphenylbi-smuth. Challenger and co-workers⁴ have shown that triphenylbi-smuth difluoride is the most stable of a series of compounds like $(C_6H_5)_3BiX_2$ where X is halogen or a pseudo-halogen. Second, the almost quantitative yield of diphenyl- α -naphthylbi-smuth from diphenyl- α -naphthylbi-smuth dichloride is additional evidence^{4a} for the stability of this unsymmetrical organobi-smuth compound.

The smooth and rapid reactions leading to excellent yields of R_3Bi compounds, suggest that the procedure might also be applicable to variously substituted organobi-smuth halides, as well as to analogous arsenicals and antimonials. By analogy with the related reaction with mercurials³ it is altogether probable that reducing agents related to hydrazine also may be used effectively.

Other reagents have been used for the conversion of organobi-smuth halides to R_3Bi compounds: hydrogen sulfide,⁵ ammonium sulfide,⁶ moist silver oxide,^{7a,b} alcoholic ammonia,⁸ sodium hydrosulfite, formaldehyde, sodium and alcohol, and dimethyl sulfate and alkali.⁹ Of these, the most successful one was sodium hydrosulfite which gave about 80% yields of triphenylbi-smuth and tri-*p*-tolylbi-smuth from the corresponding R_3BiCl_2 compounds. Unfortunately, secondary reactions took place with nitro-nuclear types.

Experimental Part

Two typical experimental procedures follow.

Conversion of Diphenylbi-smuth Chloride to Triphenylbi-smuth.—To a solution of 2.0 g. (0.04 mole) of hydrazine hydrate in 60 cc. of absolute alcohol contained in a 200-cc. three-necked flask equipped with mechanical stirring, was added 4.0 g. (0.01 mole) of diphenylbi-smuth chloride.

Reaction occurred immediately. Stirring at room temperature was continued for an hour, after which the reaction mixture was heated to boiling and filtered. The insoluble material was once again extracted with hot alcohol. The alcoholic filtrate was then poured into 400 cc. of water and the precipitated triphenylbi-smuth extracted with ether. The ether extracts were dried over anhydrous sodium sulfate, and the ether distilled. The yield of triphenylbi-smuth was 2.75 g. (93.5%), m. p. 75–76°; mixed m. p. with an authentic sample, 75–76°.

Conversion of Triphenylbi-smuth Dichloride to Triphenylbi-smuth.—To a stirred suspension of 2.56 g. (0.005 mole) of triphenylbi-smuth dichloride in 60 cc. of 95% ethanol was added 2.0 g. of hydrazine hydrate. Reaction occurred immediately and the solution became yellow in color. After about a half-minute, the solution was decolorized and the triphenylbi-smuth precipitated out of solution. Stirring was continued for an hour, after which the mixture was poured into 300 cc. of water. The aqueous suspension was extracted with ether, the ether layer separated and dried, and the ether distilled. The yield was 2.1 g. (95.4%), m. p. 75–76°; mixed m. p. with triphenylbi-smuth, 75–76°.

The results are summarized in Table I. The method of mixed melting points was used to complete identity of each of the products.

TABLE I
CONVERSION OF $RBiX_2$, R_2BiX , AND R_3BiX_2 COMPOUNDS TO R_3Bi

Organobi-smuth halide	Product	Yield, %
$(C_6H_5)_2BiCl$	$(C_6H_5)_3Bi$	93.5
$C_6H_5BiBr_2^a$	$(C_6H_5)_3Bi$	81.5
$(o-CH_3C_6H_4)_3BiCl_2$	$(o-CH_3C_6H_4)_3Bi$	99.0
$(o-CH_3C_6H_4)_3BiBr_2$	$(o-CH_3C_6H_4)_3Bi$	100
$(C_6H_5)_3BiCl_2$	$(C_6H_5)_3Bi$	95.4
$(C_6H_5)_3BiBr_2$	$(C_6H_5)_3Bi$	100
$(p-CH_3C_6H_4)_3BiCl_2$	$(p-CH_3C_6H_4)_3Bi$	100
$(p-ClC_6H_4)_3BiCl_2^b$	$(p-ClC_6H_4)_3Bi$	78.0
$(C_6H_5)_3BiF_2$	$(C_6H_5)_3Bi$	97.8
$(C_6H_5)_2(C_{10}H_7(\alpha))BiCl_2$	$(C_6H_5)_2(C_{10}H_7(\alpha))Bi$	96.2

^a In this experiment, dry ether was used as a solvent.

^b This was the only reaction where decomposition was apparent. The reaction mixture was red in color, and the red tint persisted in the final product.

Summary

Hydrazine effects a smooth and rapid conversion of arylbi-smuth halides of the general types $RBiX_2$, R_2BiX and R_3BiX_2 to R_3Bi compounds in excellent yields.

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RECEIVED JANUARY 15, 1940

- (4) (a) Challenger and Wilkinson, *J. Chem. Soc.*, **121**, 91 (1922); (b) Challenger and Richards, *ibid.*, 405 (1934).
 (5) Michaelis and Polis, *Ber.*, **20**, 54 (1887).
 (6) Michaelis and Marquardt, *Ann.*, **251**, 323 (1889).
 (7) (a) Gillmeister, *Ber.*, **30**, 2843 (1897); (b) Challenger and Goddard, *J. Chem. Soc.*, **117**, 762 (1920).
 (8) Challenger and Ridgway, *J. Chem. Soc.*, **121**, 104 (1922).
 (9) Supniewski and Adams, *THIS JOURNAL*, **48**, 507 (1926).