tion that closely approaches that represented by the formula $Al_2Br_6 \cdot 6C_6H_5CH_3$.

2. When this oil is evaporated at room temperature at 10 to 11 mm. pressure the non-volatile product appears to have the formula $Al_2Br_6 \cdot C_6H_5CH_3$.

3. The results of the determination of the molecular weight of the oil indicate that the latter when dissolved was converted into toluene and the complex $Al_2Br_6 \cdot C_6H_5CH_3$.

4. The ethylation of benzene with ethyl chloride and ethyl bromide when the molecular ratio of Al_2Cl_6 to C_6H_6 was 1 to 1 gave yields of *s*-triethylbenzene from 85 to 90% of the theoretical.

5. Excellent yields of *s*-ethyldimethylbenzene and *s*-diethylmethylbenzene were obtained.

6. A series of experiments showed that the molecular ratios of Al_2Cl_6 to hydrocarbon was the determining factor in the relative proportions in which the several alkylated products were formed.

7. At 0° the chief product of the methylation of benzene with 3 moles of halide is 1,2,4-trimethylbenzene; at 100° the product is chiefly 1,3,5-trimethylbenzene.

8. The rearrangement of *o*-xylene and *p*-xylene to a mixture of the three isomers was studied.

9. The influence of temperature on the structure of the xylenes formed when toluene is methylated showed that the low temperature favors the formation of the ortho and para compounds; at 100° the chief product is the meta isomer. In ethylation the product was largely meta at the two temperatures.

10. Detailed directions are given for the preparation of the symmetrical tri derivatives because the methods give much higher yields and purer products than have been obtained in the past.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Reactivities of Organometallic Compounds. XXVI.* Interconversion of Bismuth and Alkali Metals

BY HENRY GILMAN, H. L. YABLUNKY AND A. C. SVIGOON

Interconversion reactions are related to the relative reactivities of organometallic compounds.[1] Incidental to studies on the metalation of radicals attached to heavy metals,[2] we have now observed that when triarylbismuth compounds react with organoalkali compounds the following typical interconversion occurs.

$$(p\text{-}CH_3C_6H_4)_3Bi + 3n\text{-}C_4H_9Li \longrightarrow 3p\text{-}CH_3C_6H_4Li + (n\text{-}C_4H_9)_3Bi$$

The reaction probably takes place step-wise with the intermediate formation of unsymmetrical organometallic compounds.[2] Pertinent illustrations of the formation of unsymmetrical compounds in interconversions of bismuth compounds are to be found in studies by Challenger and Ridgway.[3] These authors observed that tri-α-naphthylbismuth and diphenylmercury gave not only di-α-naphthylmercury and triphenylbismuth, but also diphenyl-α-naphthylbismuth. They also noted that triphenylbismuth and tri-α-naphthylbismuth reacted readily to give diphenyl-α-naphthylbismuth.

Tri-*p*-chlorophenylbismuth was one of the several triarylbismuth compounds examined in this study. This compound was selected because recent studies have shown that metalation of a polynuclear compound occurs preferentially in that nucleus having a so-called negative atom or group. For example, metalation of *p*-bromodiphenyl ether takes place in the bromophenyl and not in the phenyl nucleus.[4] The absence of metalation in the several typical triarylbismuth compounds investigated indicates that metalation is without promise as a possible indirect means of introducing water-solubilizing groups into triarylbismuth compounds.

The interconversion is probably an equilibrium

(*) Paper XXV, THIS JOURNAL, **61**, 957 (1939).

(1) For a general discussion of interconversion reactions of organometallic compounds, see pp. 481–485 of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938.

(2) Gilman and Bebb, THIS JOURNAL, **61**, 109 (1939).

(3) Challenger and Ridgway, *J. Chem. Soc.*, **121**, 104 (1922). These unsymmetrical compounds can be prepared conveniently in liquid ammonia by interaction of R_2BiNa with R'X compounds. The R_2BiNa compounds are first prepared from R_2BiX compounds and sodium in liquid ammonia.

(4) Gilman, Langham and Jacoby, THIS JOURNAL, **61**, 106 (1939). See, also, Wittig, Pockels and Dröge, *Ber.*, **71**, 1903 (1938); and Gilman, Cheney and Willis, THIS JOURNAL, **61**, 951 (1939).

reaction, and the rate of interconversion of triarylbismuth and organoalkali compounds is distinctly slower than with other arylmetallic compounds like those of lead.[5]

The step-wise oxidation of organometallic compounds generally gives first peroxides and then alcohols or phenols. Noteworthy exceptions are the benzylmetallic compounds of some Group V metals, which give benzaldehyde. For example, tribenzylbismuth,[3] tribenzylarsenic[6] and tribenzylamine[7] give benzaldehyde, but no benzaldehyde has been reported from the oxidation of tribenzylphosphorus[8a] or tribenzylantimony.[8b] Dibenzylzinc on oxidation gives high yields of benzyl alcohol.[9] It seems of interest to establish whether other organobismuth compounds give aldehydes on oxidation. Accordingly, the tri-*n*-butylbismuth obtained in these studies was oxidized, first by air and then by oxygen. Positive Schiff tests showed that tri-*n*-butylbismuth does give small quantities of aldehyde on oxidation. However, in attempts to get sizable quantities that could be characterized by appropriate derivatives it was observed that when a few grams of tri-*n*-butylbismuth were oxidized the reaction took place with explosive violence.

Experimental Part

All operations were carried out in a nitrogen atmosphere. The organoalkali compounds resulting from the interconversion reactions were characterized as their corresponding acids subsequent to carbonation.

Tri-*p*-tolylbismuth and *n*-Butyllithium.—A mixture of 4.82 g. (0.01 mole) of tri-*p*-tolylbismuth[10] and 0.03 mole of *n*-butyllithium (free of metallic lithium) in 100 cc. of dry ether was refluxed for twenty hours. After carbonation by powdered solid carbon dioxide there was isolated a 70% yield of *p*-toluic acid.

In another parallel experiment, the tri-*n*-butylbismuth (previously synthesized by Davies, Norvick and Jones[11]) was obtained in a 66% yield. The tri-*n*-butylbismuth was isolated by a procedure reported recently for the recovery of triethylbismuth.[12]

Two additional experiments were carried out in which the time of reaction was reduced from twenty hours to one hour. With this shorter time of reaction, the yields of *p*-toluic acid were only 17.7 and 20%, respectively.

Tri-*p*-tolylbismuth and *n*-Butylsodium.—A mixture of 25.2 g. (0.052 mole) of tri-*p*-tolylbismuth and 0.156 mole of *n*-butylsodium in 500 cc. of petroleum ether (b. p. 60–68°) was heated at about 35° for twenty hours. Carbonation was effected by gaseous carbon dioxide, using an external ice–salt bath. After filtration, the tri-*n*-butylbismuth was isolated in a 46% yield. Acidification of the lithium salts gave a 33% yield of *p*-toluic acid, together with some *n*-valeric acid.

Tri-*α*-naphthylbismuth and *n*-Butyllithium.—A mixture of *n*-butyllithium (0.03 mole) in 65 cc. of ether and 5.9 g. (0.01 mole) of tri-*α*-naphthylbismuth[13] in 100 cc. of benzene was refluxed gently for eighteen hours. Carbonation by gaseous carbon dioxide gave a 48.1% yield of *α*-naphthoic acid.

When tri-*α*-naphthylbismuth in benzene and *n*-butyllithium in benzene[14] were mixed and then refluxed gently for eighteen hours, no apparent reaction occurred. No *α*-naphthoic acid was obtained after carbonation by gaseous carbon dioxide, and the recovery of tri-*α*-naphthylbismuth was practically quantitative. The solvent apparently has a marked influence on the reaction. It is possible that appropriate solvents may make metalation possible.

Tri-*p*-chlorophenylbismuth and *n*-Butyllithium.—Tri-*p*-chlorophenylbismuth was prepared in 65% yield from *p*-chlorophenylmagnesium bromide in essential accordance with the directions for the synthesis of triphenylstibine.[10,15] A mixture of 5.43 g. (0.01 mole) of tri-*p*-chlorophenylbismuth and *n*-butyllithium (0.03 mole) in 185 cc. of ether was refluxed for twenty hours. Carbonation by powdered solid carbon dioxide gave a 90% yield of *p*-chlorobenzoic acid.

Tri-*p*-ethoxyphenylbismuth.—A mixture of 0.01 mole of tri-*p*-ethoxyphenylbismuth and 0.03 mole of *n*-butyllithium in 165 cc. of ether was refluxed for eleven hours. Carbonation gave a 27.4% yield of *p*-ethoxybenzoic acid. The tri-*p*-ethoxyphenylbismuth was prepared[10] by us in a 51.8% yield using the Grignard technique. It was made earlier in unsatisfactory yields from the bismuth–sodium alloy and *p*-bromoethoxybenzene.[16]

Tri-*o*-ethoxyphenylbismuth.—To the Grignard reagent prepared from 19.65 g. (0.105 mole) of *o*-bromoethoxybenzene and 2.5 g. of magnesium turnings in 100 cc. of ether[17] was added 9.9 g. (0.034 mole) of bismuth chloride in ether. Stirring and refluxing were continued for one hour after the addition of bismuth chloride. After cooling, hydrolysis was effected with iced water, and the ether layer

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(5) Studies by F. W. Moore. For example, the maximum interconversion of tetraphenyllead and *n*-butyllithium is reached in about one hour under conditions which require several hours for triarylbismuth compounds.

(6) Michaelis and Paetow, *Ann.*, **233**, 67 (1886).

(7) Limpricht, *ibid.*, **144**, 308 (1867).

(8) (a) Letts and Blake, *Proc. Roy. Soc.* (Edinburgh), **16**, 193 (1890); (b) Tsukervanik and Smirnov, *J. Gen. Chem.* (U. S. S. R.), **7**, 1527 (1937).

(9) Gilman and Nelson, THIS JOURNAL, **61**, **741** (1939).

(10) The tri-*p*-tolylbismuth was prepared in a 75.8% yield by using directions patterned after those applied to the synthesis of triphenylstibine [Hiers, "Organic Syntheses," Coll. Vol. I, p. 535].

(11) Davies, Norvick and Jones, *Bull. soc. chim.*, **49**, 187 (1931).

(12) Gilman and Nelson, THIS JOURNAL, **59**, 935 (1937).

(13) Prepared in 71% yield from *α*-naphthylmagnesium bromide and bismuth chloride in accordance with the procedure mentioned in ref. 10.

(14) Prepared in accordance with the directions of Ziegler and Colonius, *Ann.*, **479**, 135 (1930).

(15) Although our tri-*p*-chlorophenylbismuth was prepared in essential accordance with earlier directions [Challenger and Ridgway, *J. Chem. Soc.*, **121**, 91 (1922)], it melted at 104°. *Anal.* Calcd. for $C_{18}H_{12}Cl_3Bi$: Bi, 38.43; Cl, 19.58. Found: Bi, 38.46 and 38.65; Cl, 19.35.

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

(17) Gilman, Zoellner, Selby and Boatner, *Rec. trav. chim.*, **54**, 584 (1935).

separated. Removal of the ether left a solid which when recrystallized from hot ethanol melted at 121–122°; yield 78%.

Anal. Calcd. for $C_{24}H_{27}O_3Bi$: Bi, 36.53. Found: Bi, 36.49 and 36.77.

A mixture of 0.01 mole of tri-*o*-ethoxyphenylbismuth and 0.03 mole of *n*-butyllithium in 165 cc. of ether was refluxed for eleven hours. Carbonation gave a 64% yield of *o*-ethoxybenzoic acid, characterized by a mixed melting point determination of its menthyl ester. From this reaction as well as from the interconversion reaction with tri-*p*-ethoxyphenylbismuth, there were also formed tri-*n* butylbismuth and *n*-valeric acid.

Summary

Triarylbismuth compounds and organoalkali compounds undergo the following typical interconversion reaction

$$(p\text{-}CH_3C_6H_4)_3Bi + 3n\text{-}C_4H_9Li \longrightarrow 3p\text{-}CH_3C_6H_4Li + (n\text{-}C_4H_9)_3Bi$$

There is no evidence of nuclear metalation.

Tri-*n*-butylbismuth is oxidized with explosive violence by oxygen, and an aldehyde appears to be one of the preliminary products of oxidation.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Kinetics of the Saponification of the Ethyl Esters of Normal Aliphatic Acids

BY HILTON A. SMITH AND H. S. LEVENSON

Recently two papers have been published which deal with the effect of the length of the carbon chain in the normal aliphatic series on the kinetics of some chemical process. The first[1] deals with the base catalyzed hydrolysis or saponification of ethyl esters of a number of aliphatic acids, while the second[2] reports the study of the acid-catalyzed esterification of normal aliphatic acids with methyl alcohol. In both cases the values of the bimolecular rate constants decreased with increasing length of the carbon chain until butyric acid (or ethyl butyrate) was reached. Further lengthening of the chain had no effect on the rate constants.

While the agreement of these two papers as to the actual change in the values of k is excellent, the assignments of the variation of the value of k to the activation energy or to the steric factor in the equation $k = sZe^{-E/RT}$ are at variance with each other. Evans and co-workers state that the variation in k is due entirely to variation in the activation energy, while in the case of the esterification reactions the activation energy is found to be constant. This disagreement does not seem reasonable.

A comparison of the two studies yields the following facts. In the case of the esterification studies, the values of k were determined at four temperatures. The values were found to be in good agreement with those obtained by Williamson and Hinshelwood in the case of acetic acid[3] and by Goldschmidt in the cases of acetic, propionic, butyric and valeric acids.[4]

Since it is easily possible to make an error of a few per cent. in activation energies as determined by the graphical method, the calculation of the activation energies of the esterification reactions has been checked by the method of least squares. The values obtained in this manner are: formic, 9560; acetic, 9985; propionic, 9834; and higher acids, 9750. These values are all within a range of some 200 cal. with the exception of that for formic acid. This value is low solely for the reason that the k at 40° is low as compared to the three other values. The reaction is so fast at this temperature (half completion in two minutes) that the value may well be a little low. The value of E obtained from the three lower values of k is 9790 cal., which is in excellent agreement with the activation energies of the higher acids. It seems quite improbable that the values of E are in sufficient error to allow the variation of k to be attributed to any variation in E.

In the case of the saponification study, the values of k were determined at three temperatures only. The authors state that the plot of log k against $1/T$ gives a good straight line in each case. Their data were replotted, and the results showed their statement to be inexact for the early members of the series. There is a considerable variation between the slope of the line connecting the values of log k between 20 and 35° and that of the line connecting the values of log k between 35 and

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(1) Evans, Gordon and Watson, *J. Chem. Soc.*, 1439 (1938).

(2) Smith, THIS JOURNAL, **61**, 254 (1939).

(3) Williamson and Hinshelwood, *Trans. Faraday Soc.*, **30**, 1145 (1934).

(4) Goldschmidt and Thuesen, *Z. physik. Chem.*, **81**, 30 (1912).