[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# The Products of the Cleavage of Triarylbismuth Derivatives by –SH-Containing Compounds[1]

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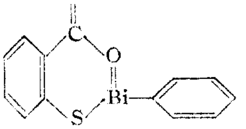
The cleavage of triarylbismuch compounds by compounds containing the –SH or –COOH groups has been investigated. The reaction leads generally to the formation of derivatives of the structure $RBi(SR')_2$ or $RBi(O_2CR'')_2$.

Incidental to a study on the rates of cleavage of organometallic compounds by –SH-containing compounds,[3] it became of interest to ascertain the structure of the compounds formed. The present study was concerned primarily with the cleavage of organo-bismuth compounds.

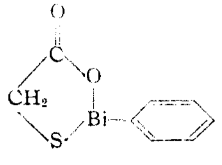
When molecular equivalents of triphenylbismuth, tri-*p*-tolylbismuth or tri-*p*-chlorophenylbismuth and thiophenol were heated, under nitrogen, in solvents like chloroform, benzene or toluene, or at 100° in the absence of solvent, the principal product was of the structure $RBi(SC_6H_5)_2$. Correspondingly, triphenylbismuth and methyl thiosalicylate gave $C_6H_5Bi(SC_6H_4CO_2CH_3\text{-}o)_2$. In all of the experiments, unreacted bismuth compound was recovered. If any $R_2BiSR'$ or $(R'S)_3Bi$ was formed, the quantities were insufficient to be detected. For purposes of identification, diphenylphenylmercaptobismuth was prepared by the reaction of diphenylbismuth chloride and thiophenol in dry ether while triphenylmercaptobismuth[4] and tri-*o*-carbomethoxyphenylmercaptobismuth were obtained by treating triphenylbismuth with a large excess of –SH compound in boiling xylene.

Tri-α-naphthylbismuth was not cleaved by thiophenol, even in boiling xylene. This anomalous behavior could not have been predicted on the basis of earlier studies on the relative labilities of organic radicals in organometallic compounds.[1] In contrast, diphenyl-α-naphthylbismuth was cleaved readily by thiophenol, in boiling chloroform, to give α-naphthyldiphenylmercaptobismuth. It should be noted that solubility[1] was not a factor in these reactions, since in both instances, the bismuth compound was in solution in the boiling solvent.

When the triphenylbismuth reacted with thiosalicylic acid, two phenyl groups were cleaved as anticipated; the product, however, was the interesting cyclic derivative



The corresponding five membered cyclic derivative,



could not be obtained in a pure state from the reaction between thioglycolic acid and triphenylbismuth.[5]

The preferential cleavage of two aryl groups from triaryl bismuth compounds seems to be general, since with molecular equivalents of benzoic and cinnamic acids, triphenylbismuth gave phenylbismuth dibenzoate and phenylbismuth dicinnamate, respectively.

Triphenylantimony was not cleaved by thiophenol after 80 minutes heating at 100°.

## Experimental Part

All experiments were conducted in an atmosphere of nitrogen. All melting points are uncorrected.

**Phenyldiphenylmercaptobismuth.**—A mixture of 4.4 g. (0.01 mole) of triphenylbismuth, 1.1 g. (0.01 mole) of thiophenol and 35 ml. of chloroform was refluxed two hours and then allowed to cool. The bright yellow solid which separated was recrystallized from chloroform to give 1.3 g. (26% yield) of product, yellow plates, m.p. 170° (with decomposition).

*Anal.* Calcd. for $C_{18}H_{15}BiS_2$: Bi, 41.45; S, 12.70. Found: Bi, 41.60; S, 12.90.

The recovery of triphenylbismuth was 1.8 g. (44%).

***p*-Tolyldiphenylmercaptobismuth.**—Tri-*p*-tolylbismuth, 2.4 g. (0.005 mole), and 0.55 g. (0.005 mole) of thiophenol were heated for one hour at 100° to give 1.02 g. (39% yield) of product, m.p. 155° (with decomposition).

*Anal.* Calcd. for $C_{20}H_{19}BiS_2$: S, 12.37. Found: S, 12.43, 12.49.

The recovery of unreacted bismuth compound was 0.92 g. (39%).

***p*-Chlorophenyldiphenylmercaptobismuth.**—A solution of 11.0 g. (0.02 mole) of tri-*p*-chlorophenylbismuth and 2.2 g. (0.02 mole) of thiophenol in 25 ml. of toluene was refluxed one hour and cooled. The yellow solid which separated was recrystallized from benzene to give 4.22 g. (39%) of product, m.p. 170° (with decomposition).

*Anal.* Calcd. for $C_{18}H_{14}BiClS_2$: Bi, 38.81; S, 11.91. Found: Bi, 39.11; S, 11.76, 11.91.

**Phenyl-di-*o*-carbomethoxyphenylmercaptobismuth.**—Heating 4.4 g. (0.01 mole) of triphenylbismuth and 1.68 g. (0.01 mole) of methyl thiosalicylate on the steam-bath for two hours gave 0.31 g. (5% yield) of product, m.p. 107–108°, after recrystallization from petroleum ether.

*Anal.* Calcd. for $C_{22}H_{19}BiO_4S_2$: Bi, 33.70. Found: Bi, 33.98, 33.94.

**Diphenylphenylmercaptobismuth.**—A stirred suspension of 2.0 g. (0.005 mole) of diphenylbismuth chloride in 50 ml. of dry ether was treated with a solution 0.55 g. (0.005 mole) of thiophenol in 25 ml. of dry ether. After several hours

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[1] Paper LXX in the series: "Relative Reactivities of Organometallic Compounds." The preceding paper with R. W. Leeper is in *J. Org. Chem.*, **16**, 466 (1951). For the preceding paper on organobismuth compounds see H. Gilman and H. L. Yale, THIS JOURNAL, **72**, 8 (1950); see, also, H. Gilman and H. L. Yale, *Chem. Revs.*, **30**, 281 (1942).

[2] E. R. Squibb & Sons, New Brunswick, N. J.

[3] H. Gilman and J. F. Nelson, THIS JOURNAL, **59**, 935 (1937).

[4] This compound was also prepared by the reaction between anhydrous bismuth chloride and thiophenol.

[5] It has been suggested that on the basis of their insolubility, these cyclic compounds may actually be polymers, *e.g.*, $(C_6H_5)_{x,x}Bi(SCH_2CO_2)_{x,x}$. Such a possibility cannot be excluded from consideration; however, generally speaking, even the bismuth salts of organic acids are quite insoluble, so that this property in itself, is not conclusive evidence.

stirring the yellow solid was filtered and recrystallized from benzene to give an 80% yield of product, m.p. 160° (with decomposition).

*Anal.* Calcd. for $C_{18}H_{15}BiS$: S, 6.78. Found: S, 6.79.

**Triphenylmercaptobismuth.**—Refluxing a mixture of 4.4 g. (0.01 mole) of triphenylbismuth, 5.5 g. (0.05 mole) of thiophenol and 25 ml. of xylene for 15 hours gave a quantitative yield of the product, needles, m.p. 90–91°, after recrystallization from absolute alcohol.

*Anal.* Calcd. for $C_{18}H_{15}BiS_3$: S, 17.93. Found: S, 17.20.

Identity was further established by a mixed m.p. with the product obtained by the reaction of anhydrous bismuth chloride and thiophenol.[4]

**Tri-*o*-carbomethoxyphenylmercaptobismuth.**—This compound was obtained in 78% yield as described above in the preparation of triphenylmercaptobismuth. The product had a m.p. of 141–143°, after recrystallization from petroleum ether.

*Anal.* Calcd. for $C_{24}H_{21}BiO_6S_3$: S, 13.52. Found: S, 13.14, 13.21.

**Phenylbismuth Thiosalicylate.**—A mixture of 4.4 g. (0.01 mole) triphenylbismuth and 1.4 g. (0.01 mole) thiosalicylic acid was heated in a graphite-bath at 150° for one hour. The fused solid was powdered, and triturated successively with hot benzene, chloroform and ether. The product was insoluble in all the solvents tested and could not be recrystallized. It did not melt up to 250°.

*Anal.* Calcd. for $C_{13}H_9BiO_2S$: Bi, 47.73. Found: Bi, 47.55.

**α-Naphthyldiphenylmercaptobismuth.**—Diphenyl-α-naphthylbismuth, 2.45 g. (0.005 mole), 0.55 g. (0.005 mole) of thiophenol and 25 ml. of chloroform were refluxed three hours, cooled, the precipitated solid filtered and recrystallized from chloroform to give 0.35 g. of α-naphthyldiphenylmercaptobismuth, which did not melt up to 240°.

*Anal.* Calcd. for $C_{22}H_{17}BiS_2$: S, 11.98. Found: S, 11.55.

The recovery of unreacted diphenyl-α-naphthylbismuth was 0.7 g.

When a mixture of 2.95 g. (0.005 mole) of tri-α-naphthylbismuth and 0.55 g. (0.005 mole) of thiophenol in 25 ml. of xylene was refluxed two hours and cooled there was recovered 2.81 g. of unreacted bismuth compound, m.p. and mixed m.p. with an authentic specimen, 229°. A qualitative test for sulfur in the recovered material was negative.

**Phenylbismuth Dicinnamate.**—When a mixture of 4.4 g. (0.01 mole) of triphenylbismuth and 1.4 g. of cinnamic acid were heated in a graphite-bath at 150°, a vigorous reaction set in and benzene refluxed. The heating was continued for 1.5 hours. The cooled mass was pulverized and triturated thoroughly with ether. The residual white powder, 1.1 g. (20% yield) which did not melt up to 230°, was insoluble in all solvents and could not be recrystallized.

*Anal.* Calcd. for $C_{24}H_{19}BiO_4$: Bi, 36.29. Found: Bi, 36.72.

The recovery of triphenylbismuth was 2.7 g. (61%).

**Phenylbismuth Dibenzoate.**—This compound was prepared in 44% yield by heating molecular equivalents of benzoic acid and triphenylbismuth for two hours on the steam-bath. The crude product was purified as above for the dicinnamate, m.p. 215–216°.

*Anal.* Calcd. for $C_{20}H_{15}BiO_4$: Bi, 39.59. Found: Bi, 40.48, 40.58.

**Cleavage of Triphenylbismuth with Thioglycolic Acid.**—The reaction was carried out between 4.4 g. of triphenylbismuth and 0.92 g. of thioglycolic acid in 25 ml. of benzene. The yellow solid was triturated with solvents as above and the product was obtained as a yellow powder.

*Anal.* Calcd. for $C_8H_7O_2SBi$: S, 8.51. Calcd. for $C_6H_9O_6S_3Bi$: S, 19.92. Found: S, 16.97.

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# Infrared Spectra of Phenols

BY R. A. FRIEDEL

Infrared spectra are presented for 22 phenols, principally the simple alkyl derivatives. The well known steric hindrance effect of ortho-substituents on the OH band is demonstrated. On the basis of the OH bands at concentrations of 4.70 mole per cent. in $CS_2$, the phenols are divided into four main classes: (1) no ortho-substituents, (2) one methyl group in the ortho position, (3) larger than methyl group in the ortho position, and (4) two methyl groups in both ortho positions. These classes differ as to band position or absorption intensity or both; intensities within a class are constant to within ±3% absorption.

The infrared spectra of various alkylphenols have been published by Whiffen and Thompson,[1] Kletz and Price,[2] Richards and Thompson,[3] and Friedel, Pierce and McGovern.[4] The present paper records the spectra of 14 alkylphenols with methyl or ethyl substituents, and 8 phenols which have larger substituents or poly-ring systems. These spectra cover the range from 7.5 to 15 microns, and from 2.5 to 3.5 microns, where investigation of intermolecular association involving the OH group can be made (Figs. 1 and 2). A method of quantitative analysis for phenol and the $C_7$ and $C_8$ alkylphenols (Fig. 1) was reported previously.[4]

Intermolecular association in phenols, and the effect of steric hindrance thereon, have been discussed by various authors. Coggeshall[5] demonstrated the strong hindrance to association of large alkyl groups, ortho to the OH, by showing the variation in spectral shifts between dilute solutions and the solid states. Richards and Thompson[3] demonstrated the same effect and gave examples showing the hindering effect of methyl groups in positions ortho to the OH. Sears and Kitchen[6] in a recent paper have achieved finer distinction between various steric hindrance effects by comparison of phenols in solution, liquid and solid states. They arrived at an empirical "hydrogen bonding index," which correlates gradual spectral shifts with methyl and larger groups in one and in both positions ortho to the OH.

## Experimental

The Perkin–Elmer Model B spectrometer was used in this work. Measurements were made in carbon disulfide solutions, concentrations of which are indicated on the spectra. Transmittance or

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(1) D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 268 (1945).

(2) T. A. Kletz and W. C. Price, *ibid.*, 644 (1947).

(3) R. E. Richards and H. W. Thompson, *ibid.*, 1260 (1947).

(4) R. A. Friedel, L. Pierce and J. J. McGovern, *Anal. Chem.*, **22**, 418 (1950).

(5) N. D. Coggeshall, THIS JOURNAL, **69**, 1620 (1947).

(6) W. C. Sears and L. J. Kitchen, *ibid.*, **71**, 4110 (1949).