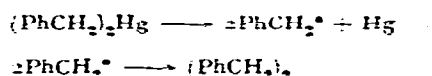


SHORT COMMUNICATIONS

Reaction of dibenzylmercury with carboxylic acids

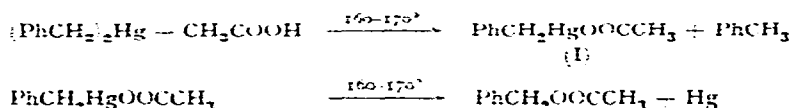
The reactions of symmetrical organomercury compounds with carboxylic acids have been studied both qualitatively¹⁻⁵ and quantitatively⁶⁻⁸. In one investigation Jones and Werner¹ showed that dibenzylmercury reacted with acetic acid at 160–170° to form mercury (98.9%), toluene, bibenzyl and benzyl acetate. The reaction was carried out in a sealed tube at 160–170° for 7 h. Under the same experimental conditions benzylmercuric acetate (I) decomposed to form mercury and benzyl acetate only¹; no bibenzyl or toluene could be found.

Dibenzylmercury is known to decompose readily on heating at 170° or above to form bibenzyl and mercury^{9,10}. The yield of mercury is quantitative and the products can be accounted for by homolysis of the mercurial:



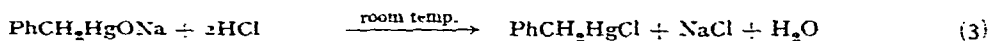
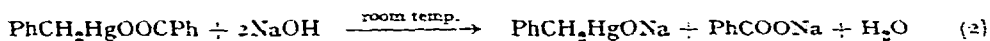
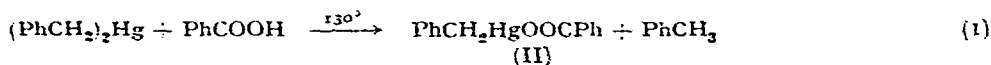
Decomposition of dibenzylmercury has now been shown to occur at lower temperatures but the rate of formation of mercury is much slower (83% mercury obtained after 12 h at 130°).

The products obtained by Jones and Werner¹ may be accounted for by postulating that two independent reactions, one homolytic and the other heterolytic, are occurring simultaneously. The homolytic reaction would give bibenzyl and some mercury and the heterolytic fission of dibenzylmercury by acetic acid would give benzylmercuric acetate (I) and toluene. At the temperature of the reaction, benzylmercuric acetate could decompose to form mercury and benzyl acetate:



Similar heterolytic fission of the mercury-carbon bonds in diphenylmercury^{2,5}, di-*o*-tolyl^{3a,b} and di-*p*-tolylmercury^{3a} has been shown to occur in their reactions with carboxylic acids, when arylmercuric carboxylates and benzene or toluene are formed, but dibenzylmercury is generally more resistant to heterolytic cleavage.

Further study of the reaction of dibenzylmercury with carboxylic acids has shown that the reaction with benzoic acid at 130° gives benzylmercuric benzoate (II) (isolated as benzylmercuric chloride) as a final reaction product. The reaction was carried out in a sealed tube at 130° for 3 h and the products isolated after decomposition and extraction were mercury (29.8%), bibenzyl, toluene and benzylmercuric chloride. The mercury and bibenzyl may be accounted for by homolysis of the mercurial as indicated above. The following reaction sequence, which involves heterolytic fission of dibenzylmercury, is proposed to explain the formation of benzylmercuric chloride from benzylmercuric benzoate (II), which was one of the final reaction products, together with toluene:



Control experiments with authentic samples of benzylmercuric benzoate and benzylmercuric hydroxide confirmed the occurrence of reactions (2) and (3). Also, when benzylmercuric benzoate was heated in a sealed tube at 130° for 3 h no decomposition occurred.

Experimental

Preparation of reagents. Dibenzylmercury (m.p. 111°) and benzylmercuric chloride (m.p. 104°), were prepared by the method of Jones and Werner¹. Benzylmercuric bromide (m.p. 119°, lit.^{11,12} 119°) was prepared similarly in 55% yield from benzylmagnesium bromide and mercuric bromide.

Benzylmercuric hydroxide (m.p. 123°: from methanol), was prepared by heating equimolar quantities of benzylmercuric chloride and sodium hydroxide in dry methanol. Its purity was determined from an estimation of its mercury content using the method of Koten and Adams¹³. (Found: Hg, 59. C₇H₈HgO calcd.: Hg, 65%.) Hence purity was 91%.)

Benzylmercuric benzoate (m.p. 76°: from methanol) was prepared by heating equimolar quantities of benzylmercuric bromide and freshly prepared silver benzoate in dry methanol. Its purity was determined from an estimation of its mercury content¹³. (Found: Hg, 46.4. C₁₄H₁₂HgO₂ calcd.: Hg, 48.6%.) Hence purity was 95.4%.)

Reaction of dibenzylmercury with benzoic acid at 130°. Dibenzylmercury (10.0 g) and benzoic acid (3.2 g) were heated in a sealed ampoule at 130° for 3 h, during which mercury was deposited. The reaction residue was extracted with anhydrous ether [extract (a)] to leave a white residue, which was soluble in chloroform [extract (b)], leaving mercury (1.56 g, 29.8%).

Chloroform was removed from extract (b) and the residue had m.p. and mixed m.p. with dibenzylmercury: 109–111°.

Extract (a) was shaken with 5 N sodium hydroxide. The sodium hydroxide extract was separated from the ether layer [extract (c)] and acidified with 5 N hydrochloric acid to give a white precipitate, which was washed with 5 N sodium hydroxide, when most of the precipitate dissolved [extract (d)], leaving a small residue. This was washed with water and recrystallised from ethanol to give benzylmercuric chloride, m.p. and mixed m.p. 104°.

Extract (c) was washed with water and dried (CaCl₂). Ether was removed and the residue was distilled to give a small amount of toluene, b.p. 108–110°, which was identified by nitration to 2,4-dinitrotoluene. The residue of the distillation solidified on cooling and it was recrystallised from methanol to give bibenzyl, m.p. and mixed m.p. 51–52°.

Extract (d) was acidified with 5 N hydrochloric acid to give a white crystalline solid, which was washed with water and recrystallised from hot water to give benzoic acid, m.p. and mixed m.p. 122°.

Reaction of benzylmercuric benzoate with sodium hydroxide. A solution of benzylmercuric benzoate (1.0 g) in ether (10 ml) was shaken with 0.5 *N* sodium hydroxide. The alkaline layer was acidified with 0.5 *N* hydrochloric acid to give a white precipitate, which was washed with 0.5 *N* sodium hydroxide solution, when most of the precipitate dissolved, leaving a small residue. This was washed with water and recrystallised from ethanol to give benzylmercuric chloride, m.p. and mixed m.p. 104°.

The alkaline solution, from which the benzylmercuric chloride had been removed, was acidified with *N* hydrochloric acid to give a white crystalline solid, which was washed with water and recrystallised from hot water to give benzoic acid, m.p. and mixed m.p. 122°.

Reaction of sodium salt of benzylmercuric hydroxide with hydrochloric acid. A solution of benzylmercuric hydroxide (1.0 g) in 5 *N* sodium hydroxide was acidified with 5 *N* hydrochloric acid to give a white solid, which was insoluble in excess 5 *N* sodium hydroxide. It was washed with water and recrystallised from ethanol to give benzylmercuric chloride, m.p. and mixed m.p. 104°.

Pyrolysis of dibenzylmercury at 130°. Dibenzylmercury (2.0 g) was heated in a sealed ampoule at 130° for 12 h, during which mercury was deposited. The reaction residue was extracted with chloroform to leave mercury (0.87 g, 83%).

Attempted pyrolysis of benzylmercuric benzoate at 130°. Benzylmercuric benzoate (1.0 g) was heated in a sealed ampoule at 130° for 3 h. There was no separation of mercury and the solid recovered had m.p. and mixed m.p. with benzylmercuric benzoate: 74-75°.

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