PYROLYSIS OF DIBENZYLMERCURY IN AROMATIC SOLVENTS

K. C. BASS
Department of Chemistry, Northampton College of Advanced Technology, London (Great Britain)
(Received November 23rd, 1964)

INTRODUCTION

Dibenzylmercury decomposes readily at 170° or above to form bibenzyl and mercury[1-3]. Similarly, photochemical decomposition of dibenzylmercury in an inert solvent (*e.g.* methanol[4] or pyridine[5]) yields bibenzyl as the only organic product and mercury. The formation of bibenzyl indicates that dibenzylmercury may be used as a thermal or photochemical source of benzyl radicals in solution; it has been used as a thermal source in studies of the reactions of benzyl radicals with substituted toluenes[6], and nitrobenzene[7], and as a photochemical source in reactions with isopropylbenzene[5].

Benzyl radicals are resonance-stabilised[8] and few reactions of them, other than dimerisation, have been recorded. Accordingly, a study was undertaken of the thermal decomposition of dibenzylmercury in organic solvents of various types in an attempt to obtain further information on the reactions of benzyl radicals in solution. Many of the organic solvents used proved to be unreactive and the only products isolated were bibenzyl and mercury. However, the decompositions in 9,10-dihydroanthracene, phenol or nitrosobenzene were more complex and these investigations are reported in this paper.

RESULTS AND DISCUSSION

*Dibenzylmercury and 9,10-dihydroanthracene**

9,10-Dihydroanthracene is a hydrogen-transfer reagent which has been used in several reactions where a hydrogen donor is required, *e.g.* the formation of quinols from quinones[10] and the hydrogenation of thiyl radicals to form thiols[11]. The thermal decomposition of dibenzylmercury in the presence of 9,10-dihydroanthracene under nitrogen gave bibenzyl (72% benzyl), mercury (98%), toluene (14% benzyl) and 9,9',10,10'-tetrahydro-9,9'-bianthryl.

The formation of bibenzyl and an almost quantitative amount of mercury indicated homolytic fission of dibenzylmercury:

$$(PhCH_2)_2Hg \longrightarrow 2PhCH_2^{\bullet} + Hg$$

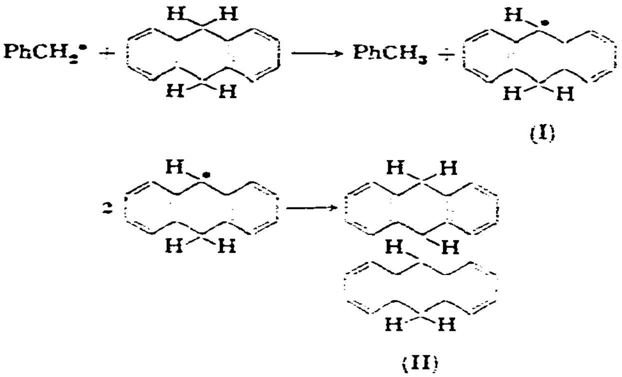
$$2PhCH_2^{\bullet} \longrightarrow PhCH_2CH_2Ph$$

The toluene may have arisen by one or both of two reactions. The first is by hydrogen abstraction from 9,10-dihydroanthracene by benzyl radicals, with simultaneous

---

* A preliminary note on the results of this reaction has been published[9].

formation of 9,10-dihydroanthryl radicals (I), which may then dimerise in solution to form 9,9',10,10'-tetrahydro-9,9'-bianthryl (II):

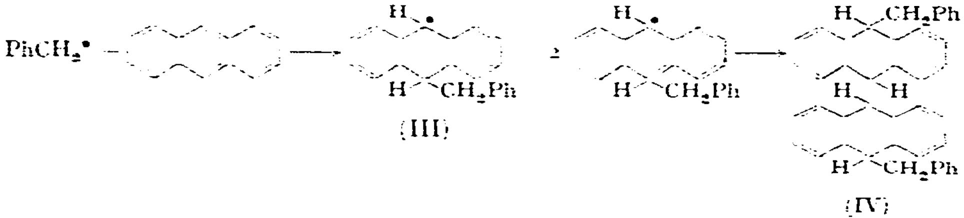


(I)

(II)

9,10-Dihydroanthryl radicals are comparatively stable radicals, which would have a high stationary concentration in solution and hence would be expected to dimerise rather than react with surrounding molecules. The dimer (II) and toluene were isolated in approximately equivalent amounts.

A similar dimerisation product was obtained by Beckwith and Waters[12] and Sisido, Udo and Nozaki[13] from the reaction of benzyl radicals with anthracene. The products included 10,10'-dibenzyl-9,9',10,10'-tetrahydro-9,9'-bianthryl (IV); this was thought to arise from dimerisation of 10-benzyl-9,10-dihydroanthryl radicals (III), which were formed by reaction of benzyl radicals with anthracene:



(III)

(IV)

Beckwith and Waters[12] generated benzyl radicals in solution by the thermal decomposition of di-*tert*-butyl peroxide in toluene and Sisido, Udo and Nozaki[13] used the thermal cleavage of tribenzyltin acetate in the presence of silver acetate.

The pyrolysis of dibenzylmercury in the presence of anthracene at 195° gives (IV)[14].

Hydrogen abstraction by benzyl radicals in solution has been observed by Hey, Shingleton and Williams[5] in the photolysis of benzylmercuric iodide in isopropylbenzene. The products were mercurous iodide, bibenzyl, 1,2,3-triphenylpropane, toluene and α,α-dimethylbibenzyl. 1,2,3-Triphenylpropane (VI), also obtained from the photolysis of dibenzylmercury in isopropylbenzene[5], was probably formed by α-hydrogen abstraction from the primary product, bibenzyl, to form toluene and 1,2-diphenylethyl radicals (V), followed by combination of benzyl and 1,2-diphenylethyl radicals:

$$\mathrm{PhCH_2\cdot + PhCH_2CH_2Ph \longrightarrow PhCH_3 + \underset{(V)}{\cdot CHPhCH_2Ph}}$$

$$\mathrm{PhCH_2\cdot + \cdot CHPhCH_2Ph \longrightarrow \underset{(VI)}{PhCH_2CHPhCH_2Ph}}$$

α,α-Dimethylbibenzyl (VIII) was formed by α-hydrogen abstraction from the solvent followed by combination of α-cumyl (α,α-dimethylbenzyl) (VII) and benzyl radicals:

$$\mathrm{PhCH_2\cdot + (CH_3)_2CHPh \longrightarrow PhCH_3 + \underset{(VII)}{\cdot C(CH_3)_2Ph}}$$

$$\mathrm{PhCH_2\cdot + \cdot C(CH_3)_2Ph \longrightarrow \underset{(VIII)}{PhCH_2C(CH_3)_2Ph}}$$

The product of dimerisation of α-cumyl radicals, bicumyl (α,α,α′,α′-tetramethylbibenzyl) was not isolated, probably because, owing to the very low stationary concentration of α-cumyl compared with that of benzyl radicals, it was formed only in very small amount. However, it was identified by gas chromatography of the products from the thermal decomposition of dibenzylmercury in isopropylbenzene[6]; bibenzyl and α,α-dimethylbibenzyl were also identified as reaction products by the same technique.

The second possible reaction for the production of toluene from the thermal decomposition of dibenzylmercury in 9,10-dihydroanthracene is the disproportionation of benzyl radicals in solution to form toluene and benzylidene diradicals, followed by dimerisation of the latter to form stilbene:

$$\mathrm{2PhCH_2\cdot \longrightarrow PhCH_3 + PhCH\!:}$$

$$\mathrm{2PhCH\!: \longrightarrow PhCH{=}CHPh}$$

This reaction might have occurred simultaneously with the formation of 9,9′,10,10′-tetrahydro-9,9′-bianthryl but there was no indication of the presence of stilbene in the reaction mixture, and the approximate equivalence of the amounts of the bianthryl derivative and toluene isolated left very little toluene to be accounted for in this way.

The disproportionation of benzyl radicals produced from the thermal decomposition of α,α′-azotoluene in boiling decalin has been reported by Bickel and Waters[15]. The products obtained from this reaction were nitrogen, bibenzyl, toluene and stilbene. Stilbene was also obtained by Horrex and Miles[16] from the gas phase pyrolysis of bibenzyl in a flow system. The reaction was interpreted as an initial α-hydrogen abstraction from bibenzyl by benzyl radicals to form toluene and 1,2-diphenylethyl radicals, but combination of benzyl and 1,2-diphenylethyl radicals did not occur under the conditions used. Disproportionation or decomposition of the 1,2-diphenylethyl radicals gave stilbene:

$$\mathrm{2PhCH_2PhCH\cdot \longrightarrow PhCH{=}CHPh + PhCH_2CH_2Ph}$$

$$\mathrm{PhCH_2PhCH\cdot \longrightarrow PhCH{=}CHPh + H\cdot}$$

Hey, Shingleton and Williams[5] have suggested that in view of their results and those of Horrex and Miles[16], it is possible that toluene and stilbene were formed from the thermal decomposition of α-α'-azotoluene by a similar mechanism to that proposed for the pyrolysis of bibenzyl.

Dibenzylmercury and phenol

The decomposition of dibenzylmercury in boiling phenol gave bibenzyl (45 % benzyl), mercury (97 %), toluene (24 % benzyl) and phenyl benzyl ether (10 % benzyl).

Bibenzyl and some of the mercury formed may be accounted for by homolytic fission of dibenzylmercury. The toluene may have been formed by one or both of two reactions. The first is by hydrogen abstraction from the hydroxyl group by benzyl radicals, followed by combination of the resulting phenoxy radicals with benzyl radicals to form phenyl benzyl ether:

$$\mathrm{PhCH_2^\bullet + PhOH \longrightarrow PhCH_3 + PhO^\bullet}$$

$$\mathrm{PhO^\bullet + PhCH_2^\bullet \longrightarrow PhOCH_2Ph}$$

However, no tarry products were formed suggesting that no oxidation of phenol had occurred, which might have been expected if there had been homolytic abstraction of hydrogen from it. The absence of tar formation is in contrast to the results of Koton and Bol'shakova[17], who studied the reactions of dibenzylmercury with substituted phenols at 100°. The products obtained were mercury, bibenzyl and unidentified tars, reported as oxidation products of the phenols, and the amounts of mercury liberated were dependent on the phenol.

An alternative origin of the toluene obtained from dibenzylmercury in phenol is by a heterolytic fission of dibenzylmercury by phenol to form benzylmercuric phenoxide and toluene:

$$\mathrm{PhCH_2HgCH_2Ph + PhOH \longrightarrow PhCH_2HgOPh + PhCH_3}$$

Similar heterolytic fission of the mercury–carbon bond in diphenylmercury occurs readily in its reactions with carboxylic acids[18, 19] at 100–130° or with phenols[18] at 100°, when phenylmercuric carboxylates or phenoxides are formed, but dibenzylmercury is generally more resistant to heterolytic cleavage. At the elevated temperature of the boiling point of a solution of dibenzylmercury in phenol, however, heterolysis might occur, and this would give toluene and benzylmercuric phenoxide. Since in the overall reaction there is a nearly quantitative yield of mercury, the benzylmercuric phenoxide, if it is formed, must decompose to give mercury and other products, possibly phenyl benzyl ether:

$$\mathrm{PhCH_2HgOPh \longrightarrow Hg + PhCH_2OPh}$$

Phenyl benzyl ether was identified by hydrolysing it with hydrochloric acid to give benzyl chloride and phenol. Thus the probable mechanism for the reaction of dibenzylmercury with phenol is that two independent reactions, one homolytic and the other heterolytic, are occurring simultaneously. The homolytic reaction gives bibenzyl and mercury and the heterolytic reaction gives toluene, mercury and phenyl benzyl ether as final reaction products.

The postulate that two independent reactions are occurring simultaneously offers an interpretation of the reaction of dibenzylmercury with acetic acid at 160–

170°, which was investigated by Jones and Werner[20]. The products were mercury (98.9 %), bibenzyl (43 % benzyl), toluene (24 % benzyl) and benzyl acetate (19 % benzyl). Homolytic fission of dibenzylmercury would give bibenzyl and mercury as for the phenol reaction, and the heterolytic reaction with acetic acid could give benzylmercuric acetate and toluene:

$$\mathrm{PhCH_2HgCH_2Ph + CH_3COOH \longrightarrow PhCH_2HgOOCH_3 + PhCH_3}$$

At the temperature of the reaction, the benzylmercuric acetate could decompose to form mercury and benzyl acetate:

$$\mathrm{PhCH_2HgOOCCH_3 \longrightarrow Hg + PhCH_2OOCCH_3}$$

Jones and Werner[20] showed that decomposition of benzylmercuric acetate under similar conditions gave only mercury and benzyl acetate; no toluene or bibenzyl was formed. Reaction of dibenzylmercury with benzoic acid at 130° gives benzylmercuric benzoate (isolated as benzylmercuric chloride) as a final reaction product[21]. The other products obtained were mercury (29.8 %), bibenzyl and toluene. Also, when benzylmercuric benzoate was heated alone under the same conditions, no decomposition occurred. These results are in accord with the suggested reaction scheme for the reaction of dibenzylmercury with acetic acid at 160–170°.

*Dibenzylmercury and nitrosobenzene**

The reaction of dibenzylmercury with nitrobenzene has been investigated by Goble, Lidstone and Pauwels[7]. The principal products were mercury (98 %), bibenzyl (28 % benzyl), benzylaniline (18 % benzyl), benzyl alcohol and benzaldehyde (determined together as benzoic acid: 37 % benzyl); small amounts of benzylideneaniline and an unidentified green solid were also obtained. The benzyl alcohol (isolated as the 3-nitrophthalate) accounted for 8.5–9.5 % of the benzyl originally present. Bibenzyl and mercury were accounted for by homolytic fission of dibenzylmercury and the following scheme was proposed to account for the other principal products:

$$\mathrm{PhNO_2 + PhCH_2^{\bullet} \longrightarrow PhNO + PhCH_2O^{\bullet}} \quad (1)$$

$$\mathrm{PhNO + 2PhCH_2^{\bullet} \longrightarrow PhN^{\bullet}CH_2Ph + PhCH_2O^{\bullet}} \quad (2)$$

$$\mathrm{PhN^{\bullet}CH_2Ph + PhCH_2O^{\bullet} \longrightarrow PhNHCH_2Ph + PhCHO} \quad (3)$$

$$\mathrm{2PhCH_2O^{\bullet} \longrightarrow PhCH_2OH + PhCHO} \quad (4)$$

As nitrosobenzene is postulated as an intermediate in this scheme the reaction of dibenzylmercury with nitrosobenzene was investigated.

Decomposition of dibenzylmercury in the presence of nitrosobenzene at 185–190° under nitrogen gave: mercury (98 %), bibenzyl (52 % benzyl), benzaldehyde [probably with some benzyl alcohol (although none was detected): determined together as benzoic acid: 18 % benzyl] and small amounts of benzylaniline (isolated as the N-nitroso derivative), aniline (isolated as phenylazo-2-naphthol), an unidentified green solid, and a considerable amount of unidentified tar.

The reaction scheme given above requires that the reaction of dibenzylmercury with nitrosobenzene should give half the amount of benzoic acid (from benzaldehyde

---

* A preliminary note on the results of this reaction has been published[22].

and benzyl alcohol) obtained from the nitrobenzene reaction. Also, the molar ratio of benzoic acid to benzylaniline should be 1:1 since there is only one benzyloxy radical produced for each benzylphenylnitrogen radical [see reaction (2) above]. The expected amount of benzoic acid (18 % benzyl) was isolated, but only a small amount of benzylaniline could be obtained (as the *N*-nitroso derivative). The precise reason for the failure to isolate it in quantity is not certain; benzylaniline did not react with nitrosobenzene under the conditions of the experiment.

Much of the product from the reaction of dibenzylmercury with nitrosobenzene was a tar. Nitrosobenzene is itself readily converted into a tar at high temperatures. In contrast, the nitrobenzene reaction did not produce any tar. The conditions in the two reactions are very different. In the nitrosobenzene reaction much nitrosobenzene is always present and part of it is undoubtedly giving a tar, whereas in the nitrobenzene reaction the nitrosobenzene probably reacts as fast as it is formed.

EXPERIMENTAL

Preparation of reagents

Dibenzylmercury[20] (m.p. 111°), 9,10-dihydroanthracene[23] (m.p. 108–109°), nitrosobenzene[24] (m.p. 66–67°; from ethanol) and phenyl benzyl ether[25] (m.p. 39°, b.p. 119–120°/3.5 mm) were prepared by established methods. 9,9',10,10'-Tetrahydro-9,9'-bianthryl (m.p. 249°) was prepared from anthrone by reduction to 9,9'-bianthryl with zinc and hydrochloric acid in acetic acid solution[26], followed by further reduction with sodium amalgam (4 % sodium) and ethanol[27].

Pyrolysis of dibenzylmercury in the presence of 9,10-dihydroanthracene

Dibenzylmercury (12 g, 0.03 mole) and 9,10-dihydroanthracene (11.5 g, 0.06 mole) were heated together under dry nitrogen (freed from oxygen with Fieser's solution[28] and dried over potassium hydroxide and magnesium perchlorate). The temperature of the reaction mixture was maintained at 210–215°, and volatile compounds were allowed to distil out. After 10 min during which mercury was deposited, the solution became slightly discoloured and 1.3 g of liquid had collected in the receiver. This was redistilled to give toluene (0.8 g, 14 % benzyl), b.p. 109–110°, which was identified by nitration to 2,4-dinitrotoluene.

The reaction residue, which solidified on cooling, was extracted with anhydrous ether to leave mercury (6.2 g, 98 %). Ether was evaporated from the extract, and the white solid residue was steam-distilled, to give a distillate as a colourless oil which solidified to a white solid, (A), and to leave a residue, (B).

The solid, (A), was filtered off and dried, and a little more of it was obtained from the mother liquors by extraction with ether, drying of the ether extracts ($MgSO_4$) and removal of the ether. The total weight of solid (a mixture of 9,10-dihydroanthracene and bibenzyl) was 12.6 g (m.p.: softened at 72° and melted completely at 93°). 9,10-Dihydroanthracene was removed from it by oxidation to anthraquinone with chromium trioxide in glacial acetic acid at room temperature. The white solid was suspended in a mixture of glacial acetic acid (25 ml) and concentrated sulphuric acid (3 ml) and a solution of chromium trioxide (6.3 g) in water (7 ml) was added slowly to the stirred suspension. A yellow solid separated from the reaction mixture, which was poured into 2 *N* sulphuric acid. The yellow precipitate was filtered off, washed with water and dried. The dry solid smelt strongly of bibenzyl. (Pure bibenzyl was unaffected by this oxidation procedure.) It was triturated with petroleum ether (b.p. 60-80°) and the solvent was removed from the extract to leave a partly solid residue, which was crystallised from methanol to give bibenzyl (4.1 g, 72 % benzyl), m.p. and mixed m.p. 51–52°.

The residue, (B), from the steam-distillation was filtered off, dried and crystallised from benzene to give a white solid (1.5 g), m.p. 249°, which was identified as 9,9'-10,10'-tetrahydro-9,9'-bianthryl by (*i*) mixed m.p. 249° (lit.[27] 248–249°), (*ii*) combustion analysis (Found: C, 93.9; H, 6.1. $C_{28}H_{22}$ calcd.: C, 93.85; H, 6.15 %.) and (*iii*) conversion to 9,10-dibromoanthracene (yellow needles from xylene), m.p. and mixed m.p. 224°, by reaction with bromine in carbon disulphide[27].

Pyrolysis of dibenzylmercury in the presence of phenol

Dibenzylmercury (10 g, 0.03 mole) and phenol (5.6 g, 0.06 mole) were boiled together and volatile compounds were allowed to distil out. After 10 min, during which mercury was deposited, the solution became slightly discoloured and 2.1 g of liquid had collected in the receiver. This was dissolved in ether and extracted with 2 *N* sodium hydroxide to remove any phenol. The ether layer was washed with water, dried ($CaCl_2$) and the ether removed to leave a residue, which was redistilled to give toluene (1.2 g, 24 % benzyl) b.p. 109–110°, identified by nitration to 2,4-dinitrotoluene.

The reaction residue, which solidified on cooling, was extracted with anhydrous ether to leave mercury (5.1 g, 97 %). The ether solution was extracted with 2 *N* sodium hydroxide to remove all unreacted phenol. A small portion of it was washed with water, dried ($CaCl_2$) and the ether removed to leave a yellow oil, which was dissolved in ethanol and diluted with water. No precipitate was formed on the addition of bromine water.

The ether solution was washed with water, dried ($CaCl_2$) and the ether removed to leave a yellow oil, which smelt strongly of bibenzyl, but would not solidify at —10°. It was heated under reflux for 10 min with a mixture of ethanol (5 ml) and concentrated hydrochloric acid (5 ml) and then cooled to give a colourless solid, which was filtered off, washed with water and crystallised from methanol to give bibenzyl (2.1 g, 45 % benzyl) m.p. and mixed m.p. 51–52°. The mother liquors were diluted with water and treated with bromine water to give a precipitate, which was washed with water and crystallised from aqueous methanol to give 2,4,6-tribromophenol, m.p. and mixed m.p. 94–95°.

Unreacted phenol in the reaction residue had been removed by extraction with sodium hydroxide and the phenol present after treatment of the yellow oil with ethanolic hydrochloridic acid was formed by the hydrolysis of a phenol derivative. It was identified as phenyl benzyl ether in another experimental run by hydrolysing the ether to benzyl chloride and phenol with a mixture of concentrated hydrochloric acid and glacial acetic acid. Benzyl chloride and phenol were not isolated but were converted to *S*-benzylthiuronium picrate and phenyl benzoate, respectively, in amounts corresponding to 1.9 g (10 % benzyl) of phenyl benzyl ether.

Further evidence for the presence of a phenolic ether in the yellow oil was obtained from the infrared absorption spectra in the range 1330–1000 cm^{-1} of the following samples (0.1 g in 1 ml of carbon tetrachloride): (*a*) bibenzyl, (*b*) phenyl benzyl ether, (*c*) a fused mixture of phenyl benzyl ether (5 %) and bibenzyl and (*d*) the yellow oil. A strong band at 1230 cm^{-1}, characteristic of aryl and aralkyl ethers[29], was present in the spectra of (*b*), (*c*) and (*d*) and absent from the spectrum of (*a*).

Pyrolysis of dibenzylmercury in the presence of nitrosobenzene

Dibenzylmercury (15 g, 0.04 mole) and nitrosobenzene (8.4 g, 0.08 mole) were heated together at 185–190° under oxygen-free, dry nitrogen. After 2 min, during which mercury was deposited, a brown tar remained. It was extracted with anhydrous ether to leave mercury (7.7 g, 98 %). The ether solution was extracted with 2 *N* hydrochloric acid and the aqueous and ether layers were treated separately.

The aqueous layer was made alkaline with 2 *N* sodium hydroxide and extracted with ether. The ether extract was washed with water, dried ($CaCl_2$), and most of the ether was removed. The residue was shaken with a few drops of concentrated hydrochloric acid and cooled to 0°. An ice-cold aqueous solution of sodium nitrite was added and the small amount of solid which precipitated was filtered off, washed with water and crystallised from aqueous ethanol to give *N*-nitrosobenzylaniline, m.p. and mixed m.p. 57–58°. The filtrate from the crude *N*-nitrosobenzylaniline was added to an ice-cold solution of 2-naphthol in 2 *N* sodium hydroxide. A red precipitate was formed, which was filtered off, washed with water and crystallised from ethanol to give 1-phenylazo-2-naphthol, m.p. and mixed m.p. 130–131°.

The ether layer was washed successively with 10 % sodium carbonate and water and dried ($CaCl_2$). The ether was evaporated to leave a brown tar, which was steam-distilled to give a distillate as an orange oil, with the characteristic odour of benzaldehyde. (The colour may have been due to traces of azobenzene, but no attempt was made to isolate it.) The residue, which consisted of a brown tar, together with traces of a dark green solid, was not further investigated. Benzaldehyde was identified from the orange oil by formation of benzaldehyde 2,4-dinitrophenylhydrazone. (The presence of benzaldehyde and traces of aniline in the reaction mixture suggested that there may have been some benzylideneaniline in the original reaction residue before extracting it with hydrochloric acid.)

The amount of benzaldehyde (and undetected benzyl alcohol) present in the orange oil was determined by oxidation. Sodium hydroxide (2 *N*, 50 ml) was added to the oil and 0.5 g portions of potassium permanganate were added to the stirred mixture until excess was present (2.5 g of potassium permanganate added). Excess of oxidant was reduced by the addition of a few drops of ethanol, and the mixture was filtered to remove manganese dioxide. The manganese dioxide and the filtrate were washed or extracted with ether and the ether solutions were combined, washed with water and dried ($CaCl_2$). The ether was removed to leave a low-melting solid, which was crystallised from methanol to give bibenzyl (3.7 g, 52 % benzyl), m.p. and mixed m.p. 51–52°.

The filtrate from the oxidation was reduced by evaporation and acidified with concentrated hydrochloric acid to give benzoic acid, which was washed with water and crystallised from hot water. Yield: 1.7 g (18 % benzyl), m.p. and mixed m.p. 122°.

SUMMARY

The thermal decomposition of dibenzylmercury in the presence of 9,10-dihydroanthracene, phenol or nitrosobenzene has been studied. The products from the 9,10-

dihydroanthracene and nitrosobenzene reactions are consistent with homolysis of dibenzylmercury to form mercury and benzyl radicals in solution and stabilisation of the latter by dimerisation or by hydrogen abstraction from 9,10-dihydroanthracene or by oxygen transfer from nitrosobenzene. Mechanisms are proposed and discussed for these reactions. A dual mechanism is proposed to account for the products of the phenol reaction: homolysis of dibenzylmercury gives bibenzyl and mercury and heterolysis of the mercurial by solvent molecules accounts for the other reaction products.

REFERENCES

1 F. C. Whitmore, *Organic Compounds of Mercury*, The Chemical Catalogue Co., New York 1921.
2 (a) G. A. Razuvaev and M. M. Koton, *Zh. Obshch. Khim.*, 1 (1931) 864; *Ber.*, 65 (1932) 613.
(b) M. M. Koton, *Dokl. Akad. Nauk SSSR*, 88 (1953) 991; *Chem. Abstr.*, 48 (1954) 8727.
3 E. Krause and A. V. Grosse, *Die Chemie der Metall-organischen Verbindungen*, Bornträger, Berlin, 1937, p. 177.
4 G. A. Razuvaev and Yu. A. Ol'dekop, *Zh. Obshch. Khim.*, 19 (1949) 1487; *J. Gen. Chem. USSR*, 19 (1949) 1489; *Chem. Abstr.*, 44 (1950) 3451.
5 D. H. Hey, D. A. Shingleton and G. H. Williams, *J. Chem. Soc.*, (1963) 1958.
6 R. A. Jackson, *J. Chem. Soc.*, (1963) 5284.
7 A. G. Goble, A. G. Lidstone and P. J. S. Pauwels, *Chem. Ind. (London)*, (1959) 1489.
8 G. W. Wheland, *Resonance in Organic Chemistry*, Wiley, New York, 1955, p. 386 and p. 401.
9 K. C. Bass, *Nature*, 201 (1964) 700.
10 E. A. Braude, L. M. Jackman and R. P. Linstead, *J. Chem. Soc.*, (1954) 3548, 3564.
11 A. F. Bickel and E. C. Kooyman, *Nature*, 170 (1952) 211.
12 A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, (1957) 1001.
13 K. Sisido, Y. Udo and H. Nozaki, *J. Am. Chem. Soc.*, 82 (1960) 434.
14 K. C. Bass and P. Nababsing, *Chem. Ind. (London)*, (1965) 307.
15 A. F. Bickel and W. A. Waters, *Rec. Trav. Chim.*, 69 (1950) 312.
16 C. Horrex and S. E. Miles, *Discussions Faraday Soc.*, 10 (1951) 187.
17 M. M. Koton and A. A. Bol'shakova, *Zh. Obshch. Khim.*, 18 (1948) 1290; *Chem. Abstr.*, 43 (1949) 1740.
18 A. G. Goble, Ph.D. Thesis, Univ. of London, 1955.
19 M. M. Koton, *Zh. Obshch. Khim.*, 9 (1939) 912; *Chem. Abstr.*, 34 (1940) 392.
20 L. W. Jones and L. Werner, *J. Am. Chem. Soc.*, 40 (1918) 1257.
21 K. C. Bass, *J. Organometal. Chem.*, 4 (1965) 92.
22 K. C. Bass, *Chem. Ind. (London)*, (1964) 1712.
23 K. C. Bass, *Org. Syn.*, 42 (1962) 48.
24 G. H. Coleman, C. M. McCloskey and F. A. Stuart, *Org. Syn.*, Collective Vol. 3 (1955) 668.
25 S. G. Powell and R. Adams, *J. Am. Chem. Soc.*, 42 (1920) 656.
26 E. de B. Barnett and M. A. Matthews, *J. Chem. Soc.*, (1923) 390.
27 H. Sachse, *Ber.*, 21 (1888) 2512.
28 L. F. Fieser, *J. Am. Chem. Soc.*, 46 (1924) 2639.
29 L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen, London, 2nd ed., 1958, p. 117.