811. *The Reaction of Benzyl Radicals with Anthracene* [1]

By K. C. BASS and P. NABABSING

The thermal decomposition of dibenzylmercury affords a convenient source of benzyl radicals. These react with anthracene at the *meso*-positions, giving 9-benzylanthracene, 9,10-dibenzylanthracene, 9,10-dibenzyl-9,10-dihydroanthracene, and 10,10′-dibenzyl-9,9′,10,10′-tetrahydro-9,9′-bianthryl.

ANTHRACENE has been shown to be reactive to a number of free radicals,[2-6] including the benzyl radical.[7-9] It has therefore been used in various reactions to trap free radicals which are formed as intermediates. The independent existence of the free radicals has been established by isolation of derivatives of anthracene, which were formed from attack on the *meso*-positions of the hydrocarbon by the radicals.

The reaction of benzyl radicals with anthracene has been investigated by Norman and Waters,[7] Beckwith and Waters,[8] and Sisido, Udo, and Nozaki.[9] Norman and Waters [7] used the cobalt chloride-catalysed reaction of benzylmagnesium chloride with benzyl chloride in ether as their source of benzyl radicals, and Beckwith and Waters [8] used the thermal decomposition of di-t-butyl peroxide in toluene.[10] Sisido, Udo, and Nozaki [9] used two sources: (*a*) treatment of benzyl chloride with iron powder in hot water and (*b*) the thermal cleavage of tribenzyltin acetate in the presence of silver acetate. The

[1] See K. C. Bass and P. Nababsing, *J. Soc. Chem. Ind.*, 1965, 307.
[2] I. M. Roitt and W. A. Waters, *J.*, 1952, 2695.
[3] A. H. Turner and W. A. Waters, *J.*, 1956, 879.
[4] A. L. J. Beckwith and W. A. Waters, *J.*, 1956, 1108.
[5] R. O. C. Norman and W. A. Waters, *J.*, 1958, 167.
[6] A. F. Bickel and E. C. Kooyman, *Rec. Trav. chim.*, 1952, **71**, 1137.
[7] R. O. C. Norman and W. A. Waters, *J.*, 1957, 950.
[8] A. L. J. Beckwith and W. A. Waters, *J.*, 1957, 1001.
[9] K. Sisido, Y. Udo, and H. Nozaki, *J. Amer. Chem. Soc.*, 1960, **82**, 434.
[10] J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 1336.

principal reaction products obtained from these investigations were the following substituted anthracenes:

9-Benzylanthracene [9] * (I)
9,10-Dibenzylanthracene [7–9]* (II)
9,10-Dibenzyl-9,10-dihydroanthracene [7–9] † (III)
9,9,10-Tribenzyl-9,10-dihydroanthracene [8,9] * (IV)
Stereoisomeric 10,10′-dibenzyl-9 9′,10,10′-tetrahydro-9,9′-bianthryls (V) [m. p.s 182—183°,[7] 227—228° [9] † (227—229°,[7] 228—229° [9] *), 238—240°,[7,9] 252° [8]]

* Obtained from tribenzyltin acetate reaction only. † Obtained from benzyl chloride–iron powder reaction only.

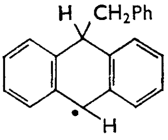
The thermal decomposition of dibenzylmercury affords a convenient source of benzyl radicals,[11-14] and it was thought to be of interest to investigate the pyrolysis of the mercurial in the presence of anthracene and compare the results with those obtained previously.[7-9]

The reaction of dibenzylmercury with anthracene gave bibenzyl (36% benzyl), mercury (98%), 9-benzylanthracene (I), 9,10-dibenzylanthracene (II), 9,10-dibenzyl-9,10-dihydroanthracene (III), 10,10′-dibenzyl-9,9′,10,10′-tetrahydro-9,9′-bianthryl (V) (m. p. 238—240°), and anthraquinone. The organic reaction products were separated and purified by chromatography on alumina, followed by recrystallisation.

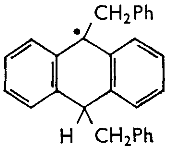
The formation of some bibenzyl, and an almost quantitative yield of mercury, indicated homolytic fission of dibenzylmercury,

$$(\mathrm{PhCH_2})_2\mathrm{Hg} \longrightarrow 2\mathrm{PhCH_2}\cdot + \mathrm{Hg}$$
$$2\mathrm{PhCH_2}\cdot \longrightarrow \mathrm{PhCH_2}\cdot\mathrm{CH_2Ph}$$

The formation of the anthracene derivatives (with the exception of anthraquinone, which was probably formed by photo-oxidation during the chromatographic separations) may be represented by the sequence of reactions postulated by Beckwith and Waters,[8] in which the benzyl radical and radicals (VI) and (VII) are suggested as active intermediates.



(VI)



(VII)

In their original reaction scheme, Beckwith and Waters [8] showed two ways by which the radical (VII) may be formed: one is by the addition of benzyl radicals to 9-benzylanthracene (I), and the other is by abstraction of hydrogen from 9,10-dibenzyl-9,10-dihydroanthracene (III) by benzyl radicals. Although 9-benzylanthracene (I) was not isolated, they suggested that the addition reaction is the more probable, because it is known that compounds such as 9,10-dibenzyl-9,10-dihydroanthracene (III) are resistant to hydrogen-abstraction by free radicals.[15]

Thus, the isolation of 9-benzylanthracene (I) from the reaction of dibenzylmercury with anthracene supports the postulate that it is an intermediate in the reaction of benzyl radicals with anthracene.

The various forms of 10,10′-dibenzyl-9,9′,10,10′-tetrahydro-9,9′-bianthryl (V) which have been isolated (see Table) are probably geometrical isomers differing in their configurations at the *meso*-carbon atoms.[7] Three isomers of the bianthryl (V) were isolated from the cobalt chloride-catalysed reaction of benzylmagnesium chloride with benzyl chloride in ether in the presence of anthracene.[7] Hence it would seem that, at the low

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[11] A. G. Goble, A. G. Lidstone, and P. J. S. Pauwels, *J. Soc. Chem. Ind.*, 1959, 1489.
[12] R. A. Jackson, *J.*, 1963, 5284.
[13] K. C. Bass, *Nature*, 1964, **201**, 700.
[14] K. C. Bass, *J. Soc. Chem. Ind.*, 1964, 1712.
[15] E. C. Kooyman and A. Strang, *Rec. Trav. chim.*, 1953, **72**, 342.

temperature of boiling ether, the dimerisation of radical (VI) to form the bianthryl (V) is not stereospecific.[7] Only one isomer (m. p. 238—240°) of the bianthryl was obtained in the present work. This isomer was presumably one of higher thermal stability, since the reaction of dibenzylmercury with anthracene was carried out at 190—195°. Norman and Waters [7] have shown that the lower-melting isomers of the bianthryl (m. p. 182—183° and 227—229°) are converted into the higher-melting isomer when heated above their melting points.

A similar dimerisation product was obtained from the thermal decomposition of dibenzylmercury in the presence of 9,10-dihydroanthracene.[13] The reaction involved abstraction of hydrogen from 9,10-dihydroanthracene by benzyl radicals to form toluene and 9,10-dihydroanthryl radicals, which dimerised to form 9,9',10,10'-tetrahydro-9,9'-bianthryl.

EXPERIMENTAL

Reagents.—Dibenzylmercury [16] (m. p. 111°), 9-benzylanthracene [17] (m. p. 133—134°), and 9,10-dibenzyl-9,10-dihydroanthracene [18] (m. p. 119°) were prepared by established methods.

Chromatographic alumina (Hopkin and Williams: "Camag," M.F.C., Brockmann Activity 2, alkaline) was used in the hydrocarbon separations.

Pyrolysis of Dibenzylmercury in the Presence of Anthracene.—Dibenzylmercury (5 g., 0·013 mole) and anthracene (2·3 g., 0·017 mole) were heated together at 190—195°. After 3 min., during which mercury was deposited, a clear residue remained and solidified on cooling. It was extracted with benzene to leave mercury (2·57 g., 98%). The benzene was removed and the residue was extracted with light petroleum (b. p. 40—60°) to leave unchanged anthracene (0·83 g.).

The petroleum extract was chromatographed on alumina and elution with light petroleum gave bibenzyl (0·86 g.), m. p. and mixed m. p. 51—52° (from methanol). Elution with 6 : 1 light petroleum–benzene gave 9-benzylanthracene [9] (0·03 g.), m. p. and mixed m. p. 133—134° (from acetone), $\lambda_{\text{max.}}$ (EtOH) 257 (ε 113,000), 332 (ε 2725), 348 (ε 5320), 366 (ε 9200), and 385 (ε 8645) mμ.

Continued elution with 6 : 1 solvent gave a yellow oil. It was extracted with hot methanol, leaving an oily residue. The solvent was evaporated to leave a solid, which was crystallised from methanol to give 9,10-dibenzyl-9,10-dihydroanthracene (0·36 g.), m. p. and mixed m. p. 119° [Found: C, 92·8; H, 6·9%; *M* (ebullioscopic in acetone), 366. Calc. for $C_{28}H_{24}$: C, 93·3; H, 6·7%; *M*, 360], $\lambda_{\text{max.}}$ (EtOH) 208 (ε 37,160), 260 (ε 2330), 263 (ε 2520), and 272 (ε 1080) mμ. The yellow oily residue remaining after the methanol extraction was dissolved in benzene and rechromatographed on alumina. Elution with benzene gave 9,10-dibenzylanthracene (0·05 g.), m. p. and mixed m. p. 246° (from methyl acetate), $\lambda_{\text{max.}}$ ($CHCl_3$) 265 (ε 66,500), 343 (ε 2865), 360 (ε 4500), 380 (ε 7000), and 400 (ε 7040) mμ.

Elution with 2 : 1 light petroleum–benzene gave 10,10'-dibenzyl-9,9',10,10'-tetrahydro-9,9'-bianthryl (0·07 g.), m. p. 238—240° (from methanol) (lit.,[7,9] 238—240°), $\lambda_{\text{max.}}$ (EtOH) 243 (ε 2870), 248 (ε 2990), 251 (ε 3360), and 260 (ε 1385) mμ.

Finally, elution with benzene gave anthraquinone (0·05 g.), m. p. and mixed m. p. (sealed tube) 285—286° (from methyl acetate).

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[16] L. W. Jones and L. Werner, *J. Amer. Chem. Soc.*, 1918, **40**, 1257.

[17] E. de B. Barnett, J. W. Cook, and J. L. Wiltshire, *J.*, 1927, 1724.

[18] E. Bergmann and S. Fujise, *Annalen*, 1930, **480**, 188.