J. Chem. Soc. (C), 1969

## The Reactions of Benzyl and Phenyl Radicals with Fluorene and of Benzyl Radicals with Pyrene

By K. C. Bass and G. M. Taylor, Department of Chemistry, The City University, St. John Street, London, E.C.1

Benzyl radicals, generated by the pyrolysis of dibenzylmercury, react with fluorene to give 9-benzylfluorene, 9,9-dibenzylfluorene, and 9,9'-bifluorenyl. Phenyl radicals, generated by the pyrolysis of diphenylmercury, react with fluorene to give 9-phenylfluorene and 9,9'-bifluorenyl. Homolytic benzylation of pyrene gives 1-benzyl-pyrene and 1,1'-bipyrenyl.

The mechanisms for the formation of the products are discussed.

IN a previous paper <sup>1</sup> we reported the reactions of benzyl and phenyl radicals (generated by the thermal decompositions of dibenzylmercury and diphenylmercury) with indene. It was thought to be of interest to study the reactions of these radicals with fluorene, which is similar to indene in having a reactive methylene group. The reaction of benzyl radicals with pyrene, which was previously reported by Norman, Thompson, and Waters,<sup>2</sup> has also been investigated.

*Fluorene.*—The pyrolysis of dibenzylmercury in the presence of fluorene gave mercury, bibenzyl, toluene, 9-benzylfluorene, 9,9-dibenzylfluorene, 9,9'-bifluorenyl, and traces of 1,2,3-triphenylpropane and 1,2,3-triphenylpropene.

<sup>1</sup> K. C. Bass and P. Nababsing, *J. Chem. Soc.* (C), 1966, 2019. <sup>2</sup> R. O. C. Norman, G. A. Thompson, and W. A. Waters, *J. Chem. Soc.*, 1958, 175. The formation of bibenzyl and an almost quantitative yield of mercury indicated homolytic fission of dibenzylmercury. 9,9'-Bifluorenyl and 9-benzylfluorene may be accounted for by hydrogen abstraction by benzyl radicals from position 9 in fluorene to give toluene and the radical (I; R = H), followed by dimerisation of (I)



or reaction of (I) with a benzyl radical. Hydrogen abstraction by benzyl radicals from position 9 in

509

9-benzylfluorene and reaction of the resulting radical (I;  $R = PhCH_{2}$ ) with a benzyl radical would give 9,9-dibenzylfluorene. 1,2,3-Triphenylpropane was formed by  $\alpha$ -hydrogen-abstraction from the primary product, bibenzyl, by benzyl radicals to give toluene and 1,2-diphenylethyl radicals, followed by combination of the latter with benzyl radicals.<sup>3,4</sup> Further  $\alpha$ -hydrogenabstraction from 1,2,3-triphenylpropane would give 1,2,3-triphenylpropyl radicals, which may dispropor tionate to 1,2,3-triphenylpropane and 1,2,3-triphenylpropene.

Homolytic benzylation of fluorene at position 9 is analogous to the reaction of benzyl radicals with indene at position 1, which gave 1-benzylidene and 1,1'-biindenvl.<sup>1</sup>

The pyrolysis of diphenylmercury in the presence of fluorene gave mercury, biphenyl, benzene, 9-phenylfluorene, and 9,9'-bifluorenyl. The formation of mercury and biphenyl indicated homolytic fission of diphenylmercury. Phenyl radicals abstracted hydrogen from position 9 in fluorene to give benzene and the radical (I; R = H), which reacted with a phenyl radical to give 9-phenylfluorene or dimerised to 9,9'-bifluorenyl.

Pyrene.-Norman, Thompson, and Waters<sup>2</sup> have shown that benzyl radicals, generated by the thermal decomposition of di-t-butyl peroxide in toluene, react with pyrene to give 1-benzylpyrene in 3.4% yield, with 75% recovery of pyrene. They suggested that this result indicated that benzyl radicals attack pyrene at position 1, as in structure (II) (the odd electron being distributed between position 6 and others in the molecule), *i.e.*, at the carbon atom having the maximum free-valence number, which occurs at the four equivalent positions, 1, 3, 6 and 8.<sup>5</sup> Abstraction of hydrogen from (II) gives 1-benzylpyrene. A similar mechanism has been proposed for benzyl radical substitution at carbon atoms in anthracene,<sup>6</sup> acridine,<sup>7</sup> indole,<sup>8</sup> and indene.<sup>1</sup>

The pyrolysis of dibenzylmercury in the presence of pyrene gave mercury, bibenzyl, toluene, 1-benzylpyrene (4% benzyl), 1,1'-bipyrenyl, and traces of 1,2,3-triphenylpropane and 1,2,3-triphenylpropene. Dibenzylpyrenes (1,6- and 1,8-) were shown to be absent. The formation of 1,1'-bipyrenyl is of interest, as it indicates that benzyl radicals also abstracted hydrogen from position 1 in pyrene to give 1-pyrenyl radicals, which dimerised in solution.

The results of Norman, Thompson, and Waters<sup>2</sup> and of the present work show that pyrene is not very reactive towards homolytic attack, in accordance with its moderate methyl radical affinity.<sup>9</sup>

- <sup>4</sup> K. C. Bass and P. Nababsing, *J. Chem. Soc.* (C), 1966, 1184. <sup>5</sup> G. Berthier, C. A. Coulson, H. H. Greenwood, and A. Pullman, Compt. rend., 1948, 226, 1906.
- (a) A. L. J. Beckwith and W. A. Waters, J. Chem. Soc., 1957, 1001; (b) K. C. Bass and P. Nababsing, J. Chem. Soc.,
- 1965, 4396. 7 W. A. Waters and D. H. Watson, J. Chem. Soc., 1957, 253.
  - <sup>8</sup> J. Hutton and W. A. Waters, J. Chem. Soc., 1965, 4253.

EXPERIMENTAL

Reagents.-Dibenzylmercury 10 (m.p. 111°), 9-benzylfluorene <sup>11</sup> (m.p.  $134^{\circ}$ ), 9,9-dibenzylfluorene <sup>12</sup> (m.p.  $147^{\circ}$ ), 1-benzylpyrene<sup>2</sup> (m.p. 89-90°), 1,6-dibenzylpyrene<sup>2</sup> (m.p. 194°), 1,8-dibenzylpyrene<sup>2</sup> (m.p. 187°), 1,1'-bipyrenyl<sup>13</sup> (m.p. 322°, lit.,<sup>13</sup> 327-328°), 1,2,3-triphenylpropane <sup>14</sup> (b.p. 220-230°/10 mm.), and 1,2,3-triphenylpropene 15 (m.p. 62-63°) were prepared by established methods.

9-Phenylfluorene was prepared by the reaction of 9-potassiofluorene with bromobenzene in boiling dioxan, and crystallised from methanol (m.p. 145-146°, lit.,<sup>16</sup> 146.5-147°). Diphenylmercury (Koch-Light) was crystallised from benzene (m.p. 124-125°). 9,9'-Bifluorenyl (Aldrich) was crystallised from ethanol-benzene (m.p. 242-243°).

Gas Chromatography.-The Perkin-Elmer Model 800 Chromatograph with a column of 15% silicone elastomer on Celite 545 (72-85 mesh) was employed. Compounds were identified by comparison of retention times with those of authentic samples.

Pyrolysis of Dibenzylmercury in the Presence of Fluorene.-Dibenzylmercury (1 g.) and fluorene (5 g.) were heated together under reflux, in an atmosphere of nitrogen, for 5 min. at 190-195°. The residue was extracted with ether to leave mercury (0.51 g., 98%). Gas chromatography of the ether solution indicated the presence of bibenzyl (59% benzyl), toluene (10% benzyl), 9-benzylfluorene (8% benzyl), 9,9-dibenzylfluorene, 9,9'-bifluorenyl, and traces of 1,2,3-triphenylpropane and 1,2,3-triphenylpropene.

Pyrolysis of Diphenylmercury in the Presence of Fluorene.-Diphenylmercury (2 g.) and fluorene (3.8 g.) were heated together at 200-210°, in an atmosphere of nitrogen, and volatile compounds were condensed in a cold trap. After 4 hr. a light brown residue remained. A small amount of condensate was identified as benzene by gas chromatography. The residue was extracted successively with ether and carbon tetrachloride to leave mercury (0.25 g, 22%). Gas chromatography of the combined ether and carbon tetrachloride solutions indicated the presence of biphenyl, 9-phenylfluorene, and 9,9'-bifluorenyl.

Pyrolysis of Dibenzylmercury in the Presence of Pyrene.-Dibenzylmercury (1 g.) and pyrene (4 g.) were heated together under reflux, in an atmosphere of nitrogen, for 5 min. at 190-195°. The yellow residue was extracted with ether to leave mercury (0.52 g., 99%). Gas chromatography of the ether solution indicated the presence of bibenzyl (69% benzyl), toluene (14% benzyl), 1-benzylpyrene (4% benzyl), 1,1'-bipyrenyl, and traces of 1,2,3-triphenylpropane and 1,2,3-triphenylpropene. The absence of 1,6- and 1,8-dibenzylpyrene was confirmed by the appearance of new peaks when samples were added to the ether solution.

We thank the S.R.C. for the award of a Research Studentship to G. M. T.

[8/1481 Received, October 14th, 1968]

<sup>9</sup> M. Levy and M. Szwarc, J. Amer. Chem. Soc., 1955, 77,

- 1949. <sup>10</sup> L. W. Jones and L. Werner, J. Amer. Chem. Soc., 1918, 40, 1257. <sup>11</sup> Y. Sprinzak, J. Amer. Chem. Soc., 1956, 78, 466. <sup>12</sup> Sprinzak, J. Amer. Chem. Soc., 1956, 78, 466.
- 12 G. W. H. Scherf and R. K. Brown, Canad. J. Chem., 1960, 38, 697.
  - <sup>13</sup> E. Clar and O. Kühn, Annalen, 1956, 601, 181.
  - R. C. Fuson, J. Amer. Chem. Soc., 1926, 48, 2937.
    A. Orechoff, Ber., 1914, 47, 94.

  - <sup>16</sup> C. D. Hurd and J. D. Mold, J. Org. Chem., 1948, 13, 339.

<sup>&</sup>lt;sup>3</sup> D. H. Hey, D. A. Shingleton, and G. H. Williams, J. Chem. Soc., 1963, 1958.