644. *Organic Peroxides. Part III.* Di-(9-benzyl-9-fluorenyl) Peroxide: A New Source of Benzyl Radicals.*

By J. I. G. CADOGAN, D. H. HEY, and W. A. SANDERSON.

Fluorenone and bibenzyl are the main products of the decomposition of di-(9-benzyl-9-fluorenyl) peroxide in bromobenzene, pyridine, 4-picoline, thiophen, and *NN*-dimethylaniline. From the products of reactions of the peroxide with thiophen and with 4-picoline in the presence of di-t-butyl peroxide, it is concluded that free benzyl radicals are present. The mode of formation of these and other products is discussed.

SINCE the formation of free benzyl radicals by the pyrolysis of tetrabenzyltin was first reported by Paneth and Lautsch [1] they have been prepared in the gas phase by a variety of routes,[2] none of which is readily applicable to the liquid phase. Benzyl radicals in solution have been prepared by the decomposition of di(phenylacetyl) peroxide,[3] αα'-azotoluene,[4] and 1-benzyl-3-phenyltriazen,[5] by the electrolysis of benzylmagnesium bromide [6] in ether, and by fission of benzyl ethers with Grignard reagents [7] or with t-butoxy-radicals.[8] In addition, any sufficiently reactive radical, if generated in toluene solution, will abstract hydrogen from the methyl group to form a benzyl radical, and this method has been widely used for the study of the reactions of benzyl radicals.[9] The available sources of benzyl radicals are not always entirely satisfactory, since they entail either (i) the primary generation of other radicals, as in the decomposition of di-t-butyl peroxide in toluene, (ii) the use of a single substance, such as a 1-benzyl-3-aryltriazen, which produces other radicals in addition to benzyl, or (iii) the use of substances, such as αα'-azotoluene or di(phenylacetyl) peroxide, which are unstable at low temperatures. In an attempt to obtain a compound which, although stable under normal conditions of storage and purification, would decompose, on being heated, to give free benzyl radicals in high yield, the

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* Part II, *J.*, 1958, 4498.

[1] Paneth and Lautsch, *J.*, 1935, 380.

[2] Hein and Mesée, *Ber.*, 1943, **76**, 430; Szwarc, *J. Chem. Phys.*, 1949, **17**, 505; Szwarc and Taylor, *ibid.*, 1953, **21**, 1746; Horrex and Miles, *Discuss. Faraday Soc.*, 1951, **10**, 187.

[3] Kharasch, Kane, and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 1621.

[4] Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 312.

[5] Dolgoplosk, Erusalimskii, Krol, and Romanor, *Zhur. obschei Khim.*, 1954, **24**, 1775.

[6] Evans, Pearson, and Braithwaite, *J. Amer. Chem. Soc.*, 1941, **63**, 2574.

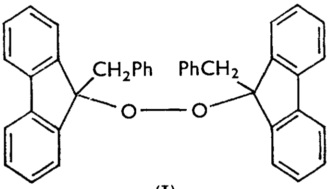
[7] Huang and Sing Sow Si-Hoe, *J.*, 1957, 3988.

[8] Huang and Sing Sow Si-Hoe, " Vistas in Free Radical Chemistry," Pergamon Press, London, 1959, p. 242.

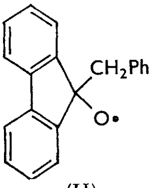
[9] (*a*) Beckwith and Waters, *J.*, 1957, 1001; (*b*) Farmer and Moore, *J.*, 1951, 131.

hitherto unknown di-(9-benzyl-9-fluorenyl) peroxide (I) has been prepared and its reactions have been studied. The peroxide was readily formed by condensing 9-benzylfluoren-9-ol with 9-benzyl-9-fluorenyl hydroperoxide in acetic acid in the presence of a small amount of sulphuric acid.

By analogy with the decomposition of related peroxides,[10,11] it would be expected that di-(9-benzyl-9-fluorenyl) peroxide would give the radical (II) on thermal decomposition in solution. In theory, this alkoxy-radical can react in three ways: (*a*) by elimination of a benzyl radical with the formation of fluorenone, (*b*) by cleavage of the five-membered ring to give an *ortho*-substituted phenyl radical (III), or (*c*) by rearrangement to a new radical (IV) which could dimerise to give a bis-dibenzyl ether. The last process resembles the well-known Wieland rearrangement of triarylmethoxy-radicals.[12]



(I)



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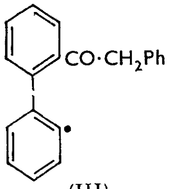
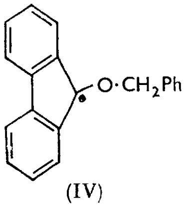


(III)



(IV)

In view of the known stability [13] of the benzyl radical, the first path appeared to be most favourable energetically.

Di-(9-benzyl-9-fluorenyl) peroxide was allowed to decompose in bromobenzene, pyridine, 4-picoline, thiophen, and *NN*-dimethylaniline, and the products were isolated and identified where possible.

EXPERIMENTAL

Chromatographic separations were carried out on activated alumina (Peter Spence & Sons, Ltd., Type " H "). Gas–liquid chromatographic determinations were carried out by using a Perkin-Elmer " Fraktometer," Model 116, fitted with a high-sensitivity, dual thermal-conductivity detector which normally gives a response proportional to molecular weight. This response was tested wherever possible by analysis of mixtures of known composition, and was satisfactory.

Solvents.—Pyridine (" AnalaR ") was dried (KOH) and fractionally distilled from barium monoxide. 4-Picoline (Hopkin and Williams Ltd.) was similarly purified, having b. p. 143°/752 mm. *NN*-Dimethylaniline (500 g.) was boiled under reflux with acetic anhydride (250 g.) for 3 hr. under nitrogen. The solution was then distilled in an atmosphere of nitrogen until the temperature of the distillate was constant (193°); the distillation was completed under reduced pressure, the fraction of b. p. 84°/15 mm. being collected and redistilled from zinc dust and stored over potassium hydroxide. Thiophen (Hopkin and Williams Ltd.) was shaken successively with 7N-hydrochloric acid, 4N-sodium hydroxide, and water, and dried ($CaCl_2$); it was fractionally distilled from sodium (b. p. 84°/765 mm.). Bromobenzene was washed with aqueous 7N-sodium hydroxide, dried (Na_2SO_4), and fractionally distilled.

Preparation of Compounds.—9-Benzylfluoren-9-ol was prepared by the method of Ullmann and von Wurstemberger.[14] The product (72%) was recrystallised from ethanol to constant m. p. 143—144°. Ullmann and von Wurstemberger [14] report m. p. 139°.

9-*Benzyl*-9-*fluorenyl hydroperoxide.* To hydrogen peroxide (86% w/w; 55 ml.), sulphuric acid (*d* 1·8; 0·25 ml.), and ether (135 ml.) was added 9-benzylfluoren-9-ol (25 g.). The mixture was stirred magnetically at room temperature for 3 hr. Special precautions against explosion were taken.* Water (200 ml.) was added, the mixture was separated, and the aqueous layer

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* It should be noted that mixtures containing organic material and hydrogen peroxide of this strength sometimes result in explosion (see Criegee and Dietrich, *Annalen*, 1948, **560**, 135), although some twenty experiments of the type described above were carried out without incident.

[10] Hawkins, *Quart. Rev.*, 1950, **4**, 251.
[11] Cadogan, Hey, and Sanderson, *J.*, 1958, 4498.
[12] Wieland, *Ber.*, 1911, **44**, 2550.
[13] See, for example, Szwarc, *Discuss. Faraday Soc.*, 1947, **2**, 39.
[14] Ullmann and von Wurstemberger, *Ber.*, 1905, **38**, 4105.

was extracted with ether. The ether solution was washed with sodium hydrogen carbonate solution and with water, and was dried ($MgSO_4$). Evaporation of the solution left a yellow gum (24 g.). Iodometric analysis by the method of Davies, Foster, and White [15] showed that it contained 75% of the hydroperoxide. Purification by recrystallisation proved to be wasteful. The crude hydroperoxide was satisfactory for the preparation of di-(9-benzyl-9-fluorenyl) peroxide.

Di-(9-*benzyl*-9-*fluorenyl*) *peroxide*. Sulphuric acid (*d* 1·8; 0·5 ml.) in acetic acid (5 ml.) was added with stirring to a solution of the crude hydroperoxide (10 g.; 75% purity) and 9-benzylfluoren-9-ol (7·5 g.) in acetic acid (35 ml.) at 0°, and the solution was left overnight at room temperature. The product was collected and washed with ethanol (10 ml.) to give *di*-(9-*benzyl*-9-*fluorenyl*) *peroxide* as a colourless amorphous powder (7 g., 50%). After crystallisation from chloroform–ethanol it had m. p. 170—170·5° (decomp.) (Found: C, 88·6; H, 5·4. $C_{40}H_{30}O_2$ requires C, 88·5; H, 5·6%). The infrared spectrum of the peroxide showed a strong peak at 10·1 μ (peroxide linkage). The peroxide is stable in the dark at room temperature but rapidly discolours in sunlight, with lowering of m. p. The peroxide is stable to detonation and liberated iodine from potassium iodide in acid only when heated.

9-*Benzyl*-9-*benzyloxyfluorene*. 9-Benzylfluoren-9-ol (1·0 g.) was added to a solution from sodium (0·085 g.) in ethanol (10 ml.) and the whole was distilled to dryness. Benzyl chloride (10 ml.) was added and the solution was boiled under reflux for 4 hr., during which a brown solid separated. The mixture was evaporated almost to dryness at 20 mm. and the residue was boiled with light petroleum (b. p. 60—80°; 50 ml.). After filtration the solution was distilled to leave an oil, which at 0·05 mm. gave the following fractions: (*a*) a colourless oil (b. p. $<90°$), (*b*) a yellow oil (0·5 g.; b. p. 90—140°), and (*c*) a yellow oil (0·4 g.; b. p. 140—150°). Infrared spectrography indicated that fraction (*a*) was benzyl chloride, fraction (*b*) was probably a mixture of fluorenone and a compound absorbing strongly at 9·13 μ and fraction (*c*) was impure 9-benzylidenefluorene (by comparison with a sample m. p. 76° prepared by heating 9-benzylfluoren-9-ol with acetic and hydrochloric acid [14]). Fraction (*b*) was chromatographed on alumina, elution with light petroleum (b. p. 60—80°)–benzene (2 : 1) giving a yellow gum (0·2 g., 15%), which crystallised from aqueous ethanol to give 9-*benzyl*-9-*benzyloxyfluorene*, m. p. 106—107° (Found: C, 89·3; H, 6·3. $C_{27}H_{22}O$ requires C, 89·5; H, 6·1%). The compound had a strong absorption peak at 9·13 μ (alkyl ether).

2-*Benzylthiophen* (b. p. 75°/0·15 mm., n_D^{25} 1·5891) was prepared by the method of Steinkopf and Hanske,[16] who reported b. p. 262—265°/765 mm. 2-Benzyl-5-chloromercurithiophen, m. p. 187—189°, was prepared by the method of Steinkopf,[17] who reported m. p. 189—191°.

3-*Benzylthiophen*. Diethyl acetosuccinate (b. p. 120—128°/0·4 mm.), from ethyl sodioacetoacetate and ethyl chloroacetate,[18] was converted into 2-benzylsuccinic acid (m. p. 160—163°) by the method of Haworth, Jones, and Way [19] who reported m. p. 157—160°. The disodium salt (10 g.) was intimately mixed with phosphorus trisulphide (B.D.H.; 15 g.), transferred to a distillation flask, and heated in a bath of Wood's metal, while a slow stream of carbon dioxide was passed through the apparatus. Reaction occurred very suddenly at 260° to give a pale yellow liquid (2 ml.), which was redistilled to give 3-*benzylthiophen* as an unstable colourless oil (1·5 g., 22%), b. p. 120°/20 mm., n_D^{25} 1·5868 (Found: C, 74·3; H, 5·85. $C_{11}H_{10}S$ requires C, 75·8; H, 5·75%). The chloromercuri-derivative, prepared as described for 2-benzylthiophen, was a colourless amorphous powder, m. p. 245—247° (from dimethylformamide–ethanol) (Found: C, 20·2; H, 1·26. $C_{11}H_8Hg_2Cl_2S$ requires C, 19·1; H, 1·7%). The analysis and the well-inown activation of the α-positions in thiophen make it evident that the product is 3-*benzyl*-2,5-*di*(*chloromercuri*)*thiophen*.

Bis-(*p*-dimethylaminophenyl)methane was prepared by Cohn's method [20] from *NN*-dimethylaniline and formaldehyde. The product crystallised from ethanol in leaflets, m. p. 89—90·5° (Pinnow [21] reported m. p. 90—91°).

Thanks are accorded to Dr. G. H. Williams for the provision of samples of 4-phenethylpyridine, m. p. 69—70°, and of 1,2-di-4′-pyridylethane, m. p. 110—111°. 4-Phenethylpyridine

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[15] Davies, Foster, and White, *J.*, 1953, 1541.

[16] Steinkopf and Hanske, *Annalen*, 1939, **541**, 238.

[17] Steinkopf, *Annalen*, 1921, 424, 23.

[18] Adkins, Isbell, and Wojcik, *Org. Synth.*, Coll. Vol. II, p. 262.

[19] Haworth, Jones, and Way, *J.*, **1943**, 10.

[20] Cohn, *Chem. Ztg.*, 1900, **24**, 564.

[21] Pinnow, *Ber.*, 1894, **27**, 3166.

picrate, crystallised from acetone, had m. p. 167—168° (Fels [22] reported m. p. 162—163°). 1,2-*Di-4′-pyridylethane dipicrate*, crystallised from dimethylformamide, had m. p. 272—273° (decomp.) (Found: C, 45·0; H, 3·1; N, 18·1. $C_{12}H_{12}N_2,2C_6H_3O_7N_3$ requires C, 44·9; H, 2·8; N, 17·5%).

Decomposition of Di-(9-*benzyl*-9-*fluorenyl*) *Peroxide in Bromobenzene and in Pyridine*.—The peroxide (2·000 g.) in bromobenzene (100 ml.) was boiled under reflux for 24 hr. under nitrogen to give a yellow solution. The bulk of the bromobenzene was removed at 20 mm., and the residue was distilled (0·05 mm.) to give a yellow semicrystalline product (1·934 g.; b. p. 75—150°) and a residue (0·0236 g.; b. p. >220°). A portion (1·002 g.) of the homogenised distillate was chromatographed on alumina. Elution with light petroleum (b. p. 60—80°) gave bibenzyl (0·250 g.), m. p. and mixed m. p. 45—52° (correct infrared spectrum). Elution with benzene (130 ml.) gave a yellow viscous oil (0·077 g.), which crystallised from ethanol to give 9-benzyl-9-benzyloxyfluorene, m. p. and mixed m. p. 104—105·5° (Found: C, 89·3; H, 6·1. Calc. for $C_{27}H_{22}O$: C, 89·5; H, 6·1%). Further elution with benzene (1 l.) gave fluorenone (0·6420 g.), m. p. and mixed m. p. 79—82° (correct infrared spectrum). Elution with methanol gave slightly impure (by infrared spectrum) 9-benzylfluoren-9-ol (0·0251 g.). The recovery from the column was 0·9941 g. (99%). When a synthetic mixture containing bibenzyl (45%), fluorenone (50%), and 9-benzylfluoren-9-ol (5%) was chromatographed as above, bibenzyl (43%), fluorenone (49%), and 9-benzylfluoren-9-ol (5%) were isolated.

A similar reaction with the peroxide (2·0247 g.) in pyridine (100 ml.) at 115° for 48 hr. gave bibenzyl (0·5250 g.; m. p. 47—50°), 9-benzyl-9-benzyloxyfluorene (0·1324 g.; m. p. 104—105·5°), fluorenone (1·2382 g.; m. p. 77—81°), and 9-benzylfluoren-9-ol (0·0932 g.).

Decomposition of Di-(9-*benzyl*-9-*fluorenyl*) *Peroxide in* 4-*Picoline*.—The peroxide (2·002 g.) was allowed to decompose in 4-picoline (100 ml.) under nitrogen for 48 hr. at 115°. The mixture was distilled to leave a residue (*ca.* 10 ml.); the fraction of b. p. <143°/760 mm. was collected separately. Carbon tetrachloride (20 ml.) was added to this low-boiling fraction, which was extracted with 7N-hydrochloric acid (5 × 50 ml.) and with water, and dried (Na_2SO_4). The carbon tetrachloride solution was boiled under reflux with a mixture of nitric acid (*d* 1·5; 4 ml.) and sulphuric acid (*d* 1·8; 4 ml.) for 2 hr. Evaporation of the solvent followed by dilution with water gave impure 2,4-dinitrotoluene (0·0047 g.).

The residue which remained after the removal of the bulk of the 4-picoline was chromatographed, and the fractions obtained on elution with light petroleum (b. p. 60—80°) (*a*), benzene (*b*), and ethanol (*c*) were distilled under reduced pressure, the 4-picoline obtained in each fraction being rejected in each case. Fraction (*a*) gave bibenzyl (0·3920 g.), b. p. 70—80°/0·05 mm., m. p. and mixed m. p. 46—50°, 9-benzyl-9-benzyloxyfluorene (0·0880 g.), m. p. and mixed m. p. 104—105·5°, and a residue (0·0177 g.), b. p. >240°/0·05 mm. Fraction (*b*) gave fluorenone (1·172 g.), m. p. and mixed m. p. 70—78°, b. p. 105/0·1 mm., and a residue (0·1163 g.), b. p. >250°/0·1 mm. Fraction (*c*) gave a brown viscous liquid (0·2288 g.), b. p. 100—120°/0·1 mm., and a residue (0·0744 g.), b. p. >250°/0·1 mm. The infrared spectrum of this distillate showed it to be largely 9-benzylfluoren-9-ol, a sample of which (m. p. and mixed m. p. 138—141°) was isolated by means of chromatography.

Decomposition of Di-(9-*benzyl*-9-*fluorenyl*) *Peroxide in* 4-*Picoline in the Presence of Di-t-butyl Peroxide*.—Di-(9-benzyl-9-fluorenyl) peroxide (3·003 g.) and di-t-butyl peroxide (6·007 g.) in 4-picoline (100 ml.) were heated at 115° under nitrogen for 48 hr. The mixture was distilled under nitrogen to leave a residue (*ca.* 15 ml.). Ether–benzene (1 : 1, 50 ml.) was added and the solution was extracted with 7N-hydrochloric acid (5 × 25 ml.). The acid extracts were washed with ether (2 × 15 ml.), and the combined ether–benzene solutions were washed with water (2 × 15 ml.), dried ($MgSO_4$), and allowed to evaporate (product A). The combined aqueous extracts were basified with sodium hydroxide at 5° and extracted with chloroform (5 × 25 ml.). The chloroform solution was dried ($MgSO_4$) and allowed to evaporate (product B).

Product A (0·9737 g.) was a mixture of colourless crystals and a yellow oil. A portion (0·8560 g.) of the homogenised product was chromatographed, as described in the previous experiments, to give bibenzyl (0·2893 g.; m. p. 47—57°), 9-benzyl-9-benzyloxyfluorene (0·1013 g.; m. p. 102—104°), fluorenone (0·1808 g.; m. p. 82—83°), and 9-benzylfluoren-9-ol (0·2603 g.; m. p. 141—143°). The identities of the products were confirmed by mixed m. p. and infrared spectrography. The recovery from the column was 0·8317 g. (97%).

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[22] Fels, *Ber.*, 1904, **37**, 2137.

Product B was distilled (0·05 mm.) to give a yellow semi-solid product C (2·479 g.; b. p. 70—110°) and a residue (2·723 g.; b. p. >110°). The residue was redistilled (0·05 mm.) to give fluorenone (0·4238 g.; b. p. 100—110°, m. p. and mixed m. p. 70—80°, correct spectrum), an orange viscous oily product D (0·9882 g.; b. p. 160—180°), and a residue (1·038 g.; b. p. >220°). A portion (1·352 g.) of the homogenised product C was chromatographed. Elution with benzene gave fluorenone (0·1984 g.; m. p. and mixed m. p. 74—81°, correct infrared spectrum); elution with benzene–chloroform (9 : 1; 3 l.) gave 4-phenethylpyridine as a pale yellow semi-solid (0·2652 g.) whose picrate had m. p. and mixed m. p. 165—167°. Further elution with benzene–chloroform (9 : 1, 800 ml.) and with chloroform (1 l.) gave 1,2-di-4′-pyridylethane (0·8187 g.), m. p. and mixed m. p. 109—111° (from ether). The recovery from the column was 1·282 g. (95%). A portion (0·9733 g.) of the homogenised product D was chromatographed. Elution with benzene gave fluorenone (0·0693 g.; m. p. and mixed m. p. 82—83°, correct spectrum). Elution with chloroform–benzene (1 : 1) gave an unidentified yellow oil (0·7730 g.), whose infrared spectrum indicated that it was derived from 4-picoline. Elution with ethanol gave a yellow oil (0·1787 g.), similar to that in the preceding fraction.

Decomposition of Di-(9-benzyl-9-fluorenyl) Peroxide in Thiophen.—The peroxide (3·495 g.) in thiophen (100 ml.) was boiled under reflux under nitrogen for 22 days. Excess of thiophen was removed under nitrogen and the residue was distilled (0·05 mm.) to give the following fractions: (*a*) a pale yellow oil (0·4120 g.; b. p. 60—70°), (*b*) fluorenone (2·092 g.; b. p. 102°; m. p. and mixed m. p. 80—83°), (*c*) a pale yellow viscous oil (0·4725 g.; b. p. 145—155°), and (*d*) a residue (0·3605 g.; b. p. >250°). A fraction of thiophen (19·0 g.) boiling immediately before fraction (*a*) was collected separately and analysed by gas–liquid chromatography. A two-metre Perkin–Elmer " C " Column (Dow Corning silicone oil D.C. 200/50cST on " Celite ") was used at 84°, column pressure 1 kg./cm.^{2} with nitrogen at a flow rate of 15·2 ml./min. as the carrier gas and detector voltage 6 v. The composition of the forerun was diethyl ether (solvent) (5·6%), thiophen (93·6%), and toluene (0·8%) with relative retention times 1 : 2·5 : 4·8. A portion of fraction (*a*) was analysed by gas–liquid chromatography, using a two-metre Perkin–Elmer " C " column at 194°, column pressure 1·2 kg./cm.^{2}, flow of nitrogen 12·8 ml./min., detector voltage 6 v. The analysis showed the presence of two major and one minor component. Comparison with authentic mixtures established that 2-benzylthiophen and bibenzyl were the major components. The composition of the mixture was 2-benzylthiophen (58·3%), bibenzyl (37·5%), unknown component (4·2%). (To obtain the last figure a molecular weight of 178, *i.e.*, midway between that of bibenzyl and 2-benzylthiophen was assumed.) The retention times were 21·9, 30·3, and 17·7 min. respectively. It was not possible to separate 2- and 3-benzylthiophen by gas–liquid chromoatography, hence the figure quoted for the 2-isomer includes any of the 3-isomer also present (see below).

The remainder of fraction (*a*) was treated with mercuric chloride solution according to the procedure described by Steinkopf,[17] which precipitated 2-benzyl-5-chloromercurithiophen, m. p. and mixed m. p. 186—187° (from toluene). The infrared spectrum of this product showed no extraneous peaks. The filtrate from the first precipitation was evaporated to dryness, the residue was extracted with boiling light petroleum (b. p. 60—80°; 50 ml.), and the extracts were chromatographed on alumina. Elution with light petroleum (b. p. 60—80°) gave bibenzyl, m. p. and mixed m. p. 47—49°. When an authentic mixture of 2- and 3-benzylthiophen, containing 5% of the 3-isomer, was submitted to the procedure used for the preparation of the chloromercuri-derivatives, the initial precipitate had m. p. 175—184°. Its infrared spectrum showed extra peaks at 11·9 and at 13·2 μ, which are present in the spectrum of the chloromercuri-derivative of the 3-isomer. The absence of these peaks in the infrared spectrum of the initially produced chloromercuri-derivative obtained from fraction (*a*), coupled with the observed greater insolubility of the mercuri-derivative of the 3-isomer, indicates that the amount of 3-benzylthiophen present, if any, is significantly less than 5%.

A portion (0·4401 g.) of the homogenised fraction (*c*) was chromatographed. Elution with light petroleum (b. p. 60—80°)–benzene (2 : 1) gave 9-benzyl-9-benzyloxyfluorene (0·3190 g.), m. p. and mixed m. p. 106—107° (from aqueous ethanol). Elution with benzene gave fluorenone (0·0303 g.). Elution with ethanol gave 9-benzylfluoren-9-ol (0·0965 g.), m. p. and mixed m. p. 142° (from aqueous ethanol). The recovery from the column was 0·4358 g. (99%).

Decomposition of Di-(9-benzyl-9-fluorenyl) Peroxide in NN-*Dimethylaniline.*—The peroxide (2·001 g.) in the amine (100 ml.) was heated at 115° under nitrogen for 48 hr. to give a brown solution. After removal of the bulk of the solvent under nitrogen, the residue (10 ml.), dissolved in benzene (80 ml.), was extracted with 7N-hydrochloric acid (4 × 30 ml.). The benzene solution was washed with water (2 × 20 ml.) and dried ($MgSO_4$). The combined aqueous extracts were basified with sodium hydroxide at 0—5° and extracted with benzene (4 × 20 ml.). These extracts were washed with water, dried ($MgSO_4$), and distilled (0·05 mm.) to give (*a*) an orange oil (0·1896 g.; b. p. 56—100°), (*b*) a pale yellow solid (0·3397 g.; b. p. 144—150°), and (*c*) a residue (0·0597 g.; b. p. >200°).

Fraction (*a*) (Found: C, 80·9; H, 8·41%), which was shown by gas–liquid chromatography to contain at least five components, three of them major, was not further investigated. Fraction (*b*) crystallised from ethanol to give bis-(*p*-dimethylaminophenyl)methane, m. p. and mixed m. p. 89—90·5° (Found: C, 80·0; H, 8·6; N, 10·9. Calc. for $C_{17}H_{22}N_2$: C, 80·3; H, 8·7; N, 11·0%). The dimethylaniline distillates were combined and boiled under reflux with acetic anhydride (100 ml.) under nitrogen for 3 hr. Distillation left a residue (10 ml.). Chloroform (100 ml.) was added and the solution was extracted with 2N-hydrochloric acid (6 × 30 ml.), and the combined acidic extracts were washed with chloroform (2 × 15 ml.). The combined chloroform extracts were washed with water and dried ($MgSO_4$). Evaporation of the chloroform left *N*-methylacetanilide (0·5490 g.), m. p. and mixed m. p. 99—102°. When pure *N*-methylacetanilide (0·5002 g.) in dimethylaniline (10 ml.) was submitted to the above procedure, *N*-methylacetanilide (0·4992 g.) was recovered. The benzene solution of the non-basic portion of the reaction product was distilled to give a yellow semi-solid (1·686 g.; b. p. 76—160°/0·05 mm.). A portion of the homogenised product (0·7008 g.) was chromatographed as described above, to give bibenzyl (0·0961 g.; m. p. 48—51°), 9-benzyl-9-benzyloxyfluorene (0·0280 g.; correct infrared spectrum), fluorenone (0·4326 g.; m. p. 77—83°), and 9-benzylfluoren-9-ol (0·1361 g.; m. p. 139—141°). The identities of the products were confirmed by mixed m. p. and infrared spectrography. The recovery from the column was 0·6883 g. (98%).

DISCUSSION

The results from the decompositions of di-(9-benzyl-9-fluorenyl) peroxide, summarised in the Table, show that the predominant reaction is decomposition of the initially produced alkoxy-radical (II) to fluorenone and a benzyl radical. In solvents such as bromobenzene, pyridine, and thiophen, this accounted for 90% or more of the peroxide, and very little abstraction of hydrogen by the radical (II), to give 9-benzyl-9-fluorenol, occurred. It appears unlikely that hydrogen-abstraction by these radicals took place at the expense of the aromatic solvent, since this would have given rise to aryl radicals and hence to binuclear products, no evidence for which was found.

*Decomposition of di-(9-benzyl-9-fluorenyl) peroxide in solution.**

Experiment no.	1	2	3	4	5	6
Solvent	Bromobenzene	Pyridine	4-Picoline	4-Picoline [1]	Thiophen	Dimethylaniline
Vol. of solvent (ml.)	100	100	100	100	100	100
Peroxide (moles × 10^3)	3·690	3·737	3·693	5·540	6·445	3·692
Temperature	156°	115°	115°	115°	84°	115°
Time (days)	1	2	2	2	22	2
Fluorenone	1·86	1·84	1·76	1·07	1·80	1·57
Bibenzyl	0·72	0·78	0·58 [4]	0·33 [5]	0·13 [6]	0·33
9-Benzyl-9-fluorenol	0·05 [3]	0·09 [3]	0·23 [3]	0·20	0·06	0·33
9-Benzyl-9-benzyloxyfluorene	0·1	0·1	0·07	0·06	0·15	0·05 [7]
Benzyl accounted for (%) [2]	85	93	77	74	55	55
Peroxide accounted for (%) [2]	96	99	94	64	75	88

* Figures, unless otherwise stated, represent moles/mole of peroxide.

[1] Di-t-butyl peroxide (4·114 × 10^{-2} mole) was also present. [2] Calc. from the weights of each product recovered, including, where found, toluene, 4-phenethylpyridine, and 2-benzylthiophen. [3] Maximum figures due to impure specimens. [4] Toluene (0·007 mole/mole of peroxide) was also formed. [5] 4-Phenethylpyridine (0·49 mole/mole of peroxide) and 1,2-di-4′-pyridylethane (3·07 moles/mole of 4-phenethylpyridine) were also formed. [6] 2-Benzylthiophen (0·22 mole/mole of peroxide) and toluene (0·25 mole/mole of peroxide) were also formed. [7] Bis-(*p*-dimethylaminophenyl)methane (0·36 mole/mole of peroxide) and *N*-methylaniline (1·00 mole/mole of peroxide) were also formed.

It is conceivable that the presence of traces of moisture or of solvent of crystallisation might account for the small amounts of 9-benzyl-9-fluorenol, but no direct evidence is available on this point.

During the decompositions in bromobenzene and in pyridine, which are inert to attack by the resonance-stabilised benzyl radical, the benzyl radicals dimerised to give bibenzyl. The experiments in these solvents do not distinguish between an intramolecular " cage " decomposition of the peroxide and the normal dimerisation of free benzyl radicals. Accordingly reactions were carried out in thiophen and in 4-picoline. The reactivity of the 2-position in the heterolytic substitution of thiophen is well known, but few homolytic reactions with thiophen have been reported.

Gomberg and Bachmann,[23] who prepared various 2-arylthiophens by the Gomberg reaction, were interested only in the preparative aspects of the reaction. More recently, Ford and McKay [24] qualitatively investigated the decomposition of dibenzoyl peroxide in thiophen and isolated 2-benzoyloxythiophen in good yield. They also reported the formation of 2-benzylthiophen in the reaction of di-t-butyl peroxide with thiophen in toluene. It is evident therefore that thiophen is also very reactive towards free radicals because, in general, homolytic benzylation and benzoyloxylation will occur to a great extent only in very reactive compounds.[9a,25] Accordingly, thiophen was employed to trap any free benzyl radicals formed during the decomposition of di-(9-benzyl-9-fluorenyl) peroxide. The isolation of 2-benzylthiophen is considered to support the conclusion that free benzyl radicals are generated in this reaction. It appears that benzylation of thiophen takes place exclusively at the 2-position and that the hydrogen displaced by this substitution is removed as toluene, probably by abstraction from a σ-complex of the type postulated [26] for homolytic arylation. It is noteworthy that in spite of the activity of thiophen a small amount of bibenzyl was still formed and that no evidence of substitution by the 9-benzylfluoren-9-oxy-radical was obtained. Ford and McKay [24] found no bibenzyl in their reaction, but they did not have our advantage of the use of gas-liquid chromatography.

From the decomposition of the peroxide in 4-picoline the main products were again fluorenone and bibenzyl. The appreciable amount of 9-benzyl-9-fluorenol also formed indicates that the alkoxy-radical (II) is itself capable of abstracting hydrogen from the reactive side chain of 4-picoline to give the alcohol and, presumably, a 4-pyridylmethyl radical. It has been shown [27] that this radical will dimerise to give 1,2-di-4′-pyridylethane or will react with a benzyl radical to give the " crossed " product, 4-phenethylpyridine. It is therefore surprising that neither product was detected in our reaction with 4-picoline. It is well-known [9,27] that the decomposition of di-t-butyl peroxide in toluene, in substituted toluenes, and in the picolines gives rise to free benzyl and free benzyl-type radicals; accordingly di-(9-benzyl-9-fluorenyl) peroxide was allowed to decompose in 4-picoline in the presence of di-t-butyl peroxide. The isolation, in this instance, of 4-phenethylpyridine together with 1,2-di-4′-pyridylethane and bibenzyl is considered to be further evidence for the existence of *free* benzyl radicals formed by the decomposition of di-(9-benzyl-9-fluorenyl) peroxide.

In the reaction of di-(9-benzyl-9-fluorenyl) peroxide with *NN*-dimethylaniline no nuclear benzylation was detected and the main reaction appeared to be the normal decomposition to give fluorenone and bibenzyl. In addition to these products, *N*-methylaniline, 9-benzyl-9-fluorenol (0·33 mole/mole of peroxide) and bis-(*p*-dimethylaminophenyl)-methane (0·36 mole/mole of peroxide) were isolated. These basic products have also been isolated from the reaction of dibenzoyl peroxide [28,29] and of cumene hydroperoxide, and

[23] Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339.

[24] Ford and McKay, *J.*, 1957, 4620.

[25] Roitt and Waters, *J.*, 1952, 2695.

[26] Rondestvedt and Blanchard, *J. Org. Chem.*, 1956, **21**, 229; Chang-Shih, Hey, and Williams, *J.*, 1959, 1871.

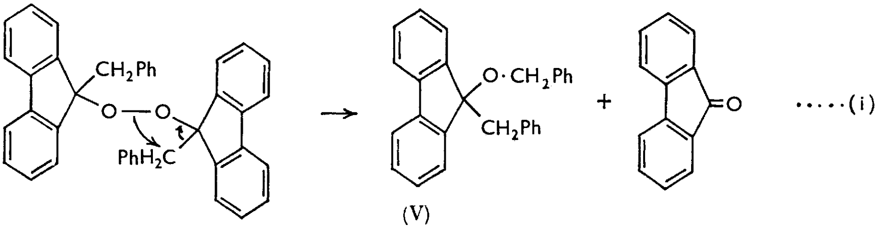
[27] Johnston and Williams, *Chem. and Ind.*, 1958, 328.

[28] Horner and Schwenk, *Angew. Chem.*, 1949, **61**, 411

[29] A. Thomas, Ph.D. Thesis, London, 1958.

NN-diphenyl-*N*′-picrylhydrazyl[29] with *NN*-dimethylaniline. Although the mechanisms of these reactions are still in doubt it appears that the first step involves bimolecular reaction of the peroxide and dimethylaniline to give an intermediate which ultimately decomposes to give formaldehyde and *N*-methylaniline, the aldehyde then reacting with *NN*-dimethylaniline to give the observed bis-(*p*-dimethylaminophenyl)methane.

It is noteworthy that, whereas the decompositions of peroxides in *NN*-dimethylaniline are different from those in other solvents, di-(9-benzyl-9-fluorenyl) peroxide appears to be an exception, both unimolecular decomposition to give fluorenone and bibenzyl and bimolecular reaction with solvent to give bis-(*p*-dimethylaminophenyl)methane, 9-benzyl-9-fluorenol, and *N*-methylaniline seem to occur simultaneously, although further experimentation with related peroxides may provide a more subtle interpretation.



(V)

·····(i)

In all the decompositions of di-(9-benzyl-9-fluorenyl) peroxide reported in this paper, small amounts of 9-benzyl-9-benzyloxyfluorene (V) were isolated. In theory this compound could arise by any of the following routes: (*a*) intramolecular breakdown of the peroxide (reaction i), (*b*) combination of a benzyl and a 9-benzylfluoren-9-oxy-radical, or (*c*) induced decomposition of the peroxide by benzyl radicals. Although the results of our experiments do not permit a decision to be made concerning the genesis of this compound, it is considered that the second alternative is least likely.

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