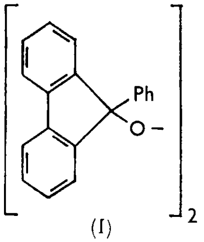
756. *Organic Peroxides. Part V.*[1] *The Decomposition of Di-(9-phenyl-9-fluorenyl) Peroxide.*

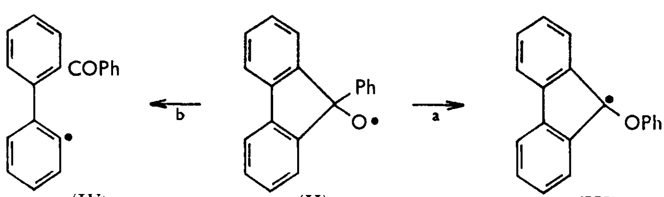
By J. I. G. CADOGAN, D. H. HEY, and W. A. SANDERSON.

Thermal decomposition of di-(9-phenyl-9-fluorenyl) peroxide in cumene gives 9-phenylfluoren-9-ol, 2-(9-phenoxy-9-fluorenyl)-2-phenylpropane, and 9,9′-diphenoxy-9,9′-bifluorenyl. No bi-α-cumyl is formed. The corresponding decomposition in nitrobenzene is more complex and interaction with the nitro-group occurs.

ALTHOUGH many references to di-(9-phenyl-9-fluorenyl) peroxide (I) exist,[2] its thermal decomposition in solution has never been studied. In theory the peroxide might be expected to decompose to give the 9-phenylfluoren-9-oxy-radical (II), which could then react further (a) by undergoing the Wieland rearrangement [3] to give the 9-phenoxyfluorenyl radical (III), (b) by ring fission to give a 2-benzoylbiphenylyl radical (IV), or (c) by loss of a phenyl radical with the formation of fluorenone. In order to determine the actual mode of decomposition the peroxide has been allowed to decompose in cumene and in nitrobenzene, and the products of these reactions have been investigated.



(I)



(IV) (II) (III)

From the products of the decomposition in cumene it is clear that reactions (b) and (c) are not operative. The isolation of 9-phenylfluoren-9-ol indicates that hydrogen abstraction from the solvent by the 9-phenylfluoren-9-oxy-radical (II) occurs, thus releasing an equivalent amount of free αα-dimethylbenzyl radicals, which usually appear as the dimer,

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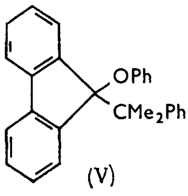
[1] Part IV, Cadogan, Hey, and Sanderson, *J.*, 1960, 4897.

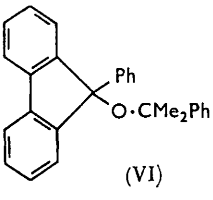
[2] (*a*) Gomberg and Cone, *Ber.*, 1906, **39**, 1461, 2957; (*b*) Staudinger, *Ber.*, 1906, **39**, 3060; (*c*) Bassey, Buncel, and Davies, *J.*, 1955, 2550.

[3] Wieland, *Ber.*, 1911, **44**, 2550.

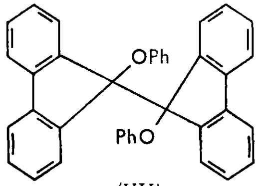
2,3-dimethyl-2,3-diphenylbutane (bi-α-cumyl). No trace of the latter was found in this case but a compound was isolated which is formulated as 2-(9-phenoxy-9-fluorenyl)-2-phenylpropane (V), formed in equivalent amount by reaction of the rearranged 9-phenylfluoren-9-oxy-radical with an αα-dimethylbenzyl radical. That the product is the isomeric



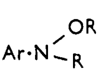
(V)



(VI)



(VII)



$Ar{\cdot}N\begin{smallmatrix}\nearrow OR\\ \searrow R\end{smallmatrix}$

(VIII)

αα-dimethylbenzyl ether (VI) of 9-phenylfluoren-9-ol cannot be entirely discounted, but Kharasch *et al.*[4] have shown that, in the decomposition of the related triphenylmethyl peroxide in cumene, αα-dimethylbenzyl radicals react exclusively with the *rearranged* alkoxy-radicals. Thus the hydrogen abstraction by the 9-phenylfluoren-9-oxy-radical competes with rearrangement to give the 9-phenoxyfluorenyl radical which does not, however, react by hydrogen abstraction, since no 9-phenoxyfluorene was detected. The isolation of 2-(9-phenoxy-9-fluorenyl)-2-phenylpropane (V), but not of bi-α-cumyl, is further evidence that reaction between unlike radicals is a favoured process.[5] The major product of the reaction is formulated as 9,9′-diphenoxy-9,9′-bifluorenyl (VII), the expected product of dimerisation of the remaining 9-phenoxyfluorenyl radicals.

The results of the decomposition in nitrobenzene are less satisfactory and the reaction is evidently complex. The main product was an intractable black solid although a small amount of 9-phenylfluoren-9-ol was isolated. It is well known [6] that more stable free radicals such as benzyl, triphenylmethyl, and 2-cyano-2-propyl radicals react with aromatic nitro-groups to give complex mixtures for which a common precursor (VIII; R = $Ph{\cdot}CH_2{\cdot}$, $Ph_3C{\cdot}$, $NC{\cdot}CMe_2{\cdot}$) has been proposed, and in this case a solid, having elemental composition corresponding to that of (VIII) (R = 9-phenoxy-9-fluorenyl) was isolated. It is therefore possible that reaction of the 9-phenoxy-9-fluorenyl radical with the nitro-group had occurred in this case, although no direct evidence is available.

EXPERIMENTAL

Nitrobenzene and cumene were purified as previously described.[7]

9-Phenylfluoren-9-ol.—The method of Arcus and Coombs [8] was used. The solvated product (m. p. 94—97·5°) crystallised from carbon tetrachloride and lost solvent of crystallisation after 90 min. at 120° to give a product, m. p. 111—112°. Arcus and Coombs, who reported m. p. 85°, noted that Ullmann and von Wurstemberger [9] reported m. p. 107°, and concluded that the product is dimorphic.

Di-(9-phenyl-9-fluorenyl) Peroxide.—9-Phenylfluoren-9-ol (20 g.) in ether (40 ml.) was stirred magnetically with 85% w/v hydrogen peroxide * (40 ml.) and sulphuric acid (0·15 ml.; *d* 1·8) for 10 hr. at room temperature. (Special precautions against explosion were taken.*) Water (100 ml.) was added and the ether layer was washed with alkali and dried ($MgSO_4$). Evaporation of the solvent left a yellow syrup (20 g.; 70% hydroperoxide content). Sulphuric acid

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

[4] Kharasch, Poshkus, Fono, and Nudenberg, *J. Org. Chem.*, 1951, **16**, 1458.

[5] Cf. McBay, Tucker, and Groves, *J. Org. Chem.*, 1959, **24**, 536.

[6] See Jackson and Waters, *J.*, 1960, 1653.

[7] Cadogan, Hey, and Sanderson, *J.*, 1958, 4498.

[8] Arcus and Coombs, *J.*, 1954, 3977.

[9] Ullmann and von Wurstemberger, *Ber.*, 1904, **37**, 73.

(1·0 ml.; *d* 1·8) in ether (10 ml.) was added to a mixture of the crude hydroperoxide (20 g.), 9-phenylfluoren-9-ol (20 g.), and acetic acid (50 ml.) in ether (50 ml.). After 15 hr. at room temperature ethanol (10 ml.) was added to precipitate crude di-(9-phenyl-9-fluorenyl) peroxide (20·5 g.), m. p. 183—187°. The peroxide crystallised in an unsolvated form (m. p. 194—195°) from *NN*-dimethylformamide. Bassey, Buncel, and Davies [2c] reported m. p. 193° for the peroxide obtained by heating the benzene-solvated product at 100°/1 mm. for 2 hr.

Decomposition of Di-(9-*phenyl*-9-*fluorenyl*) *Peroxide*.—(a) *In cumene at* 115°. The peroxide (3·026 g.) in cumene (150 ml.) was kept at 115° under nitrogen for 3 days. The bulk of the solvent was removed under nitrogen through a 25 cm. Fenske helix-packed column and suitable distillation-head. The residue (20 ml.) was cooled in ice, and the yellow solid (1·096 g.; m. p. 240—250°) which separated was collected and washed with light petroleum (b. p. 40—60°). The filtrate, on evaporation to dryness, left a residue, which was dissolved in hot benzene (15 ml.). The solid (0·07 g.) which separated was identical with the first product obtained. The benzene filtrate was chromatographed on alumina as follows: (i) light petroleum (b. p. 60—80°) gave colourless crystals (0·680 g.), m. p. 144—148°; (ii) light petroleum (b. p. 60—80°)–benzene (4 : 1) gave a colourless solid (0·310 g.) identical with the substance of m. p. 240—250° (above); (iii) benzene–chloroform (3 : 1) gave an unidentified solid (0·1 g.), m. p. 145—155°, not identical with that from fraction (i); (iv) chloroform gave an orange gum (0·964 g.).

Fraction (i) recrystallised from ethanol in needles, m. p. 147—148° (Found: C, 88·8; H, 6·4. $C_{28}H_{24}O$ requires C, 89·3; H, 6·4%). The infrared spectrum showed strong absorption at 8·0 μ and a strong triplet in the range 9·45—9·8 μ (aryl alkyl ether). By comparison with the work of Kharasch *et al.*[4] the compound is regarded as 2-(9-*phenoxy*-9-*fluorenyl*)-2-*phenylpropane*. The solids (m. p. 240—250°) initially obtained were combined with that obtained from fraction (ii) and recrystallised from chloroform–ethanol to give a product, m. p. 230—245° (decomp.) (Found: C, 85·1; H, 5·2%; *M*, 555. $C_{38}H_{26}O_2$ requires C, 88·7; H, 5·1%; *M*, 514). The substance was shown not to be solvated by the fact that no loss of weight occurred at 100°/0·1 mm. Repeated purifications by crystallisation did not improve the m. p. or analysis. The presence in the infrared spectrum of typical aryl alkyl ether peaks together with the observed molecular weight, suggested the formulation $C_{38}H_{26}O_2$, *i.e.*, the Wieland dimer, 9,9′-*diphenoxy*-9,9′-*bifluorenyl*. The product from fraction (iv) on chromatography gave 9-phenylfluoren-9-ol (0·692 g.), m. p. and mixed m. p. 109—110°, on recrystallisation from ethanol.

(b) *In nitrobenzene at* 211°. The peroxide (2·838 g.) was boiled under reflux under nitrogen in nitrobenzene for 17 hr. After being washed with dilute alkali, which extracted only a trace (0·01 g.) of acidic material, and dilute acid, the bulk of solvent was removed by distillation. Distillation (0·1 mm.) of the residue gave a red liquid (1·341 g.), b. p. 105—120°, and a residue (2·984 g.), b. p. >230°. A portion (1·329 g.) of the distillate on chromatography on alumina gave (i) nitrobenzene (0·168 g.), (ii) a yellow oil (0·694 g.), which contained three unidentified major components (by gas–liquid chromatography) which were not mononitrobiphenyls, nitrophenyl phenyl ethers, or fluorenone, and (iii) 9-phenylfluoren-9-ol (0·1 g.), m. p. and mixed m. p. 106—109°. A portion (1·302 g.) of the residue from the distillation (black crystals, m. p. 190—235°) could not be resolved by chromatography on alumina. Purification of the solid by precipitation from acetone solution by the addition of light petroleum (b. p. 40—60°) gave a *product* of m. p. 245—260° (Found: C, 85·3; H, 4·7; N, 1·5. $C_{44}H_{31}NO_3$ requires C, 85·0; H, 5·0; N, 2·2%).

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KING'S COLLEGE, STRAND, LONDON, W.C.2.

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