Aromatic Polyfluoro-compounds. Part XLIV.[1] Bis(pentafluorobenzoyl) Peroxide

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Bis(pentafluorobenzoyl) peroxide has been prepared by treatment of pentafluorobenzoyl chloride with alkaline hydrogen peroxide. It reacted with hexafluorobenzene, pentafluorobenzene, and benzene to give low yields of fluorinated biphenyls and, in each case, pentafluorophenyl pentafluorobenzoate, also in low yield.

THE reaction of aroyl peroxides with aromatics is a well known method of preparing biphenyls, although yields are often poor and much tar is formed. Williams and his co-workers have reported [2] the application of this reaction to the polyfluoroaromatic field—for example, hexafluorobenzene and benzoyl peroxide gave pentafluorobiphenyl in over 70% yield. We have prepared bis(pentafluorobenzoyl) peroxide and investigated its reactions, mainly to assess its possible utility as a synthetic reagent.

The peroxide was prepared in good yield by treatment of pentafluorobenzoyl chloride [3] with alkaline hydrogen peroxide. It decomposed under reflux in hexafluorobenzene to give mainly tar; very low yields of decafluorobiphenyl (2%) and pentafluorophenyl pentafluorobenzoate (7%) were also detected (these and other yields are based on the assumption that two moles of biaryl could be formed from one of peroxide, and one of pentafluorophenyl pentafluorobenzoate from one of peroxide). With pentafluorobenzene under reflux, biphenyls were again formed in very low yields; decafluorobiphenyl (7%), the hydrogen-replacement product, was the main one, with the fluorine-replacement products, 4*H*-nonafluorobiphenyl (2·5%) and 2*H*-nonafluorobiphenyl (0·5%) (probably), formed in lesser amounts. Pentafluorophenyl pentafluorobenzoate (12%) was again detected. Since the yields of the biphenyls were so low, there is no point in discussing the *ortho* : *para* fluorine-replacement ratio, the absence of the 3*H*-isomer, or the relative amounts of fluorine and hydrogen replacement. In both the aforementioned reactions, decafluorobiphenyl is probably a genuine homolytic aromatic substitution product and is not formed by dimerisation of two pentafluorophenyl radicals, since it was not detected in the reaction with benzene (see later). Low yields of biphenyls were also formed from the peroxide and bromopentafluorobenzene, although this reaction has not been thoroughly investigated.

It seems unlikely, therefore, that bis(pentafluorobenzoyl) peroxide is of much value for the preparation of very highly fluorinated biphenyls by use of these simple processes. It is noteworthy that pentafluorophenyl radicals, formed both by oxidation of pentafluorophenylhydrazine [4] and by photolysis of pentafluoroiodobenzene,[5] also gave very low yields of decafluorobiphenyl on treatment with hexafluorobenzene.

Better yields of a biaryl (30—40% of pentafluorobiphenyl) were obtained from the reaction of the peroxide with benzene, so the reagent may offer possibilities for the synthesis of partially fluorinated biphenyls. Pentafluorophenyl pentafluorobenzoate (3%) was again detected, together with phenyl pentafluorobenzoate (2—4%) and pentafluorobenzoic acid (25—40%). We have investigated the benzene–bis(pentafluorobenzoyl) peroxide reaction in more detail (Table). The yield of pentafluorobenzoic acid decreased with decreasing initial concentration of the peroxide, whereas the yield of pentafluorobiphenyl remained relatively constant; both characteristics have been noted before [6,7] in benzoyl peroxide decompositions in aromatic solvents. A preliminary kinetic investigation, by the method [7] of Williams and his co-workers, showed that the rate of decomposition of the peroxide in benzene at 79° varied only slightly with concentration, and that it was greater than that of benzoyl peroxide in benzene at 79°. In decomposing faster than benzoyl peroxide, bis(pentafluorobenzoyl) peroxide is unusual. It was originally [8] thought that electron-attracting substituents slowed decomposition. It was later found,[9] however, that bis-(*p*-nitrobenzoyl) peroxide and its *meta*-isomer decomposed at about the same rate as benzoyl peroxide and so this simple rule is not always followed. More thorough investigation of the kinetics of the decomposition of bis(pentafluorobenzoyl) peroxide could well be of interest.

Molarity of peroxide in benzene	0·22	0·10	0·03	0·01	0·005
Moles of pentafluorobenzoic acid [a]	0·74	0·79	0·65	0·61	0·49
Moles of pentafluorobiphenyl [a] ...	0·62	0·65	0·60	0·71	0·65
Non-volatile residue [b]	22	22	20	23	21

[a] Per mole of peroxide. [b] Wt. % of amount of peroxide used.

EXPERIMENTAL

Bis(pentafluorobenzoyl) Peroxide.—Pentafluorobenzoyl chloride [3] (9·0 g.; prepared from pentafluorobenzoic acid

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and thionyl chloride in dimethylformamide) and aqueous 2M-sodium hydroxide (20 ml.) were simultaneously added dropwise, with stirring, to a cooled (0°) solution of hydrogen peroxide (20 vol.; 40 ml.); the rates of addition were controlled to maintain alkalinity throughout the reaction. When the addition was complete (*ca.* 15 min.), the precipitate (5·5 g.) was filtered off, washed with water, and dried. This material was satisfactory for preparative experiments. Further purification was carried out by dissolving the crude material in the minimum volume of chloroform, adding twice the volume of methanol, cooling to $-40°$ and filtering quickly (recovery *ca.* 60%). *Bis(pentafluorobenzoyl) peroxide* has m.p. 72° (Found: C, 39·9; F, 45·2. $C_{14}F_{10}O_4$ requires C, 39·8; F, 45·0%).

Reactions of Bis(pentafluorobenzoyl) Peroxide.—(a) *With hexafluorobenzene.* Hexafluorobenzene (3·6 g.) and the peroxide (1·2 g.) were heated under reflux under nitrogen for 17 hr. Excess of hexafluorobenzene was distilled off and the solid residue (1·1 g.) was steam-distilled. The volatile fraction (0·1 g.) showed two peaks on g.l.c. (column of silicone gum on Celite; 180°) in a 1 : 2 area ratio. These were separated on a 40 μl. scale (collection in carbon tetrachloride solution) and shown by comparison of their i.r. spectra with those of authentic samples to be decafluorobiphenyl and pentafluorophenyl pentafluorobenzoate[10] respectively. (The ester is not appreciably hydrolysed by steam distillation.) The residue involatile in steam (1·0 g.) was a brown tar and was not investigated.

(b) *With pentafluorobenzene.* This compound (5·0 g.) and the peroxide (1·6 g.) were heated under reflux under nitrogen for 19 hr. Excess of pentafluorobenzene was distilled off and the residue (2·0 g.) was extracted with aqueous sodium hydrogen carbonate. Acidification of the aqueous solution and extraction with dichloromethane gave pentafluorobenzoic acid (0·05 g.), identified by i.r. The insoluble residue was steam-distilled and the volatile fraction (0·4 g.) was analysed and separated by g.l.c. as in (a). It consisted of (peak area ratios, expressed as %) decafluorobiphenyl (39%), 4*H*-nonafluorobiphenyl[11] (15%), 2*H*-nonafluorobiphenyl[11] (3%; identified by retention time only), and pentafluorophenyl pentafluorobenzoate[10] (43%). An attempt to separate the tarry residue (1·5 g.) into components on a silica gel column was unsuccessful.

(c) *With benzene.* Benzene (10·0 g.) (analytical grade; dried over sodium) and the peroxide (1·0 g.) were heated under reflux under nitrogen for 46 hr. Pentafluorobenzoic acid (0·4 g.) was isolated as in (b) and the steam-volatile components (0·5 g.) were separated and identified (i.r.) as in (a), as pentafluorobiphenyl (90%), pentafluorophenyl pentafluorobenzoate[10] (5%) and phenyl pentafluorobenzoate[12] (5%). The non-volatile residue (0·25 g.) was not investigated. Similar experiments (Table) at different initial concentrations of peroxide were carried out, except that the pentafluorobenzoic acid was determined by titration of the residue from the methylene chloride extraction [*cf.* (b)] with 0·02M-sodium hydroxide, and the pentafluorobiphenyl was estimated by g.l.c. (silicone gum on Celite; 180°) with nitrobenzene as internal standard. The amount of the biphenyl was always less than the amount of steam-volatile products, the difference being made up of pentafluorophenyl pentafluorobenzoate and phenyl pentafluorobenzoate. The amount of the first ester relative to the biphenyl remained approximately the same (5 : 90 by g.l.c. peak area ratio) over the whole concentration range, but the amount of the second increased from about 5 : 90 at 0·1M to 1 : 9 at 0·01M.

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