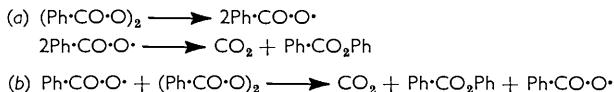


111. Homolytic Aromatic Substitution. Part XXII.* The Esters formed in the Reaction of Benzoyl Peroxide with Aromatic Solvents.

By D. I. DAVIES, D. H. HEY, and GARETH H. WILLIAMS.

When benzoyl peroxide is allowed to decompose in aromatic solvents, a little phenyl benzoate is formed together with the esters resulting from the attack of a benzoyloxy-radical on the solvent. The lactone of 2'-hydroxybiphenyl-2-carboxylic acid is also a minor product in the reaction of benzoyl peroxide with aromatic solvents.

GELISSEN and HERMANS^{1,2} studied the reaction of benzoyl peroxide with benzene and found that phenyl benzoate was a minor product. They attributed its formation to the substitution of a benzoyloxy-group for a hydrogen atom in benzene. Böeseken and Hermans³ later suggested that phenyl benzoate could also arise by the loss of a molecule of carbon dioxide from a molecule of the peroxide, a possibility also envisaged by Hey and Waters,⁴ thus: $(\text{Ph}\cdot\text{CO}\cdot\text{O})_2 \longrightarrow \text{CO}_2 + \text{Ph}\cdot\text{CO}_2\text{Ph}$. Nozaki and Bartlett⁵ studied the kinetics of the decomposition of benzoyl peroxide in organic solvents and considered that the formation of phenyl benzoate could occur either (a) by reaction between two benzoyloxy-radicals with loss of carbon dioxide, or (b) by an induced decomposition of benzoyl peroxide by means of a benzoyloxy-radical:



The reaction of benzoyl peroxide and of substituted benzoyl peroxides with benzene was further investigated by Lynch and Pausacker,^{6,7} who attempted to write balanced equations for these reactions. On the basis of these equations they concluded that phenyl benzoate is formed as a result of an intramolecular loss of carbon dioxide from the peroxide and not by the substitution of a benzoyloxy-radical for a hydrogen atom in benzene. If the mechanism postulated by Lynch and Pausacker⁶ for the formation of phenyl benzoate in the reaction of benzoyl peroxide with benzene is correct, then when a substituted benzoyl peroxide reacts with benzene the only ester formed should be that resulting from the intramolecular loss of carbon dioxide from the peroxide, *e.g.*, in the reaction of *p*-chlorobenzoyl peroxide with benzene the only ester expected would be *p*-chlorophenyl *p*-chlorobenzoate. Hydrolysis of the ester would give a single phenol which would be uncontaminated with phenol itself. In his analysis of the phenolic fraction obtained in

* Part XXI, preceding paper.

¹ Gelissen and Hermans, *Ber.*, 1925, **58**, 285.

² Gelissen and Hermans, *Ber.*, 1925, **58**, 984.

³ Böeseken and Hermans, *Annalen*, 1935, **519**, 133.

⁴ Hey and Waters, *Chem. Rev.*, 1937, **21**, 169.

⁵ Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686.

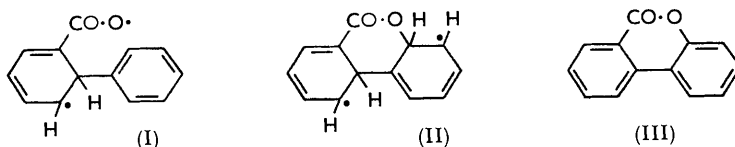
⁶ Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 40.

⁷ Pausacker, *Austral. J. Chem.*, 1957, **10**, 49.

this experiment, Pausacker ⁷ found that the results were not consistent with the hypothesis that the ester was derived entirely from the peroxide, but he did not comment on this fact. It therefore appeared desirable to investigate the extent to which esters are formed by processes (a) and (b) above, rather than by the substitution of an aryloxy-radical for a hydrogen atom of the solvent.

In a re-investigation of the reactions of benzoyl peroxide with chlorobenzene and with biphenyl it is now shown that both types of ester are formed. The products were found to contain mixtures of phenol and chlorophenols, and of phenol and hydroxybiphenyls respectively. The yield of phenyl benzoate is greater with the less reactive solvent (chlorobenzene) than with the more reactive solvent (biphenyl), which supports the mechanism of an induced decomposition, since this would be of less importance in the more reactive solvent. Further, the yield of biphenyl benzoates from the reaction of benzoyl peroxide with biphenyl is greater than the yield of chlorophenyl benzoates from the reaction with chlorobenzene. This is expected, because in the more reactive solvent (biphenyl) the benzoyloxy-radical is more likely to react with the solvent before decarboxylation.

When the esters formed in the reactions of benzoyl peroxide with chlorobenzene and with biphenyl were hydrolysed, the phenolic fraction was found to contain some high-boiling material, a component of which was found to be the lactone of 2'-hydroxybiphenyl-2-carboxylic acid. This lactone may result from loss of carbon dioxide from a molecule of



benzoyl peroxide, which can give a phenyl radical and a benzoyloxy-radical. These two radicals may react to give an intermediate (I), which subsequently becomes (II), which in turn can undergo dehydrogenation, either by the solvent or by another radical, to give the lactone (III). These reactions can be envisaged as taking place within a solvent cage. The intermediates (I) and (II) can, of course, be written in several canonical forms.

A somewhat similar mechanism for the formation of the lactone can be formulated by the attack of a phenyl radical at an *ortho*-position in a molecule of benzoyl peroxide (cf. DeTar and Weis,⁸ and Walling and Savas⁹). The appearance of the lactone in the phenolic fraction is due to its insolubility in sodium hydrogen carbonate solution.

EXPERIMENTAL

Reagents.—Benzoyl peroxide and chlorobenzene were purified as in Part II,¹⁰ and biphenyl as in Part V.¹¹ The lactone, m. p. 93.5°, of 2'-hydroxybiphenyl-2-carboxylic acid was prepared from the diazonium sulphate of anthranilic acid and phenol by the method of Graebe and Schestakow.¹²

Reaction of Benzoyl Peroxide with Chlorobenzene.—Two reactions were carried out. In reaction (I), benzoyl peroxide (25 g.) was allowed to decompose in chlorobenzene (50 g.) at 80° (thermostat) for 72 hr. In reaction (II), benzoyl peroxide (24 g.) in chlorobenzene (800 g.) was used. When the reactions were complete, the free acid was extracted with saturated aqueous sodium hydrogen carbonate, and then the excess of solvent was removed by distillation. The residue was hydrolysed for 24 hr. with boiling 2N-aqueous sodium hydroxide (200 ml.), and the "ester" acid and the phenols were isolated by standard methods. The biaryls in the neutral fraction were not isolated. The products isolated are shown in Table I.

Fraction (a) was shown to consist of a mixture of phenol and chlorophenols by a comparison

⁸ DeTar and Weis, *J. Amer. Chem. Soc.*, 1956, **78**, 4296.

⁹ Walling and Savas, *J. Amer. Chem. Soc.*, 1960, **82**, 1738.

¹⁰ Augood, Hey, and Williams, *J.*, 1952, 2094.

¹¹ Cadogan, Hey, and Williams, *J.*, 1954, 794.

¹² Graebe and Schestakow, *Annalen*, 1895, **284**, 306.

of its infrared spectrum with those of authentic specimens of phenol and the three chlorophenols, and the percentage compositions shown in Table 2 were obtained by element analyses.

In reaction (I), fraction (b) was obtained as a yellowish-white semi-solid. Successive recrystallisations from light petroleum (b. p. 80–100°) gave 2'-hydroxybiphenyl-2-carboxylic acid lactone, m. p. 91.5°, which was undepressed on admixture with an authentic specimen.¹² The two specimens had identical infrared spectra. The presence of the lactone in the phenolic fraction (b) of reaction (II) was shown by the presence of an absorption band at 5.8 μ . From both the free acid and the "ester" acid in reaction (I) it was possible to isolate, by fractional crystallisation, biphenyl-4-carboxylic acid (0.80 g., and 0.15 g. respectively), m. p. 223.5–224.5° (Found: C, 78.5; H, 5.4. Calc. for C₁₃H₁₀O₂: C, 78.8; H, 5.1%).

TABLE 1. *Yields of free acid and of the products of hydrolysis from the reaction of benzoyl peroxide with chlorobenzene.*

Reaction no.	(I)	(II)
Free acid (g.)	7.71	5.98
"Ester" acid (g.)	1.26	0.72
Phenolic fraction (a), b. p. 80–100°/20 mm. (g.)	0.164	0.184
Phenolic fraction (b), b. p. 120–130°/0.1 mm. (g.)	0.550	0.136
Non-volatile residue (g.)	0.057	0.028

TABLE 2. *Composition of phenolic fraction (a).*

Reaction no.	(I)	(II)
Chlorine (%)	11	15.2
Chlorophenols (%)	40	55
Phenol (%)	60	45

Reaction of Benzoyl Peroxide with Biphenyl.—In reaction (III), benzoyl peroxide (25 g.) was allowed to decompose in biphenyl (68.5 g.) at 80° (thermostat) for 72 hr. In reaction (IV), benzoyl peroxide (24 g.) in biphenyl (800 g.) was used. The products were worked up as described above for the reactions with chlorobenzene. In reaction (III), benzene (250 ml.) was added to the reaction mixture before the extraction of the free benzoic acid. The biaryls were not isolated. Table 3 gives the quantities of free acid and the products of hydrolysis obtained.

The phenolic fraction (a) was phenol, m. p. 43° (correct infrared spectrum). The phenolic fraction (b), which partly distilled and partly sublimed, was collected as a solid and was shown to consist mainly of hydroxybiphenyls by a comparison of its infrared spectrum with that of an authentic mixture of the isomeric hydroxybiphenyls. A weak band was observed

TABLE 3. *Yield of free acid and of the products of hydrolysis from the reaction of benzoyl peroxide with biphenyl.*

Reaction no.	(III)	(IV)
Free acid (g.)	9.67	Not estimated
"Ester" acid (g.)	1.82	1.70
Phenolic fraction (a), b. p. ca. 85°/20 mm. (g.)	0.045	0.021
Phenolic fraction (b), b. p. 90–130°/0.1 mm. (g.)	0.872	0.953
Non-volatile residue (g.)	0.137	0.100

in the spectrum at 5.8 μ , indicating the presence of 2'-hydroxybiphenyl-2-carboxylic acid lactone. This fraction, from reaction (III), was further distilled at 0.1 mm., to give: (i) at bath-temp. 100–180°, 0.25 g.; (ii) at bath-temp. 180–240°, 0.50 g.; and (iii) at bath. temp. 240–300°, 0.12 g. Fraction (i) solidified, and recrystallisation from light petroleum (b. p. 80–100°) gave 2-hydroxybiphenyl, needles, m. p. and mixed m. p. 56° (Found: C, 84.7; H, 5.8. Calc. for C₁₂H₁₀O: C, 84.7; H, 5.9%). Fraction (ii), on the evidence of its infrared spectrum, consisted of a mixture of 3- and 4-hydroxybiphenyl, and fractional crystallisation from light petroleum (b. p. 80–100°) gave 4-hydroxybiphenyl in needles, m. p. and mixed m. p. 165°. Fraction (iii) showed a strong absorption band at 5.8 μ . Several recrystallisations from light petroleum (b. p. 80–100°) gave the lactone in needles, m. p. and mixed m. p. 92.5° (Found: C, 80.0; H, 4.45. Calc. for C₁₃H₈O₂: C, 79.6; H, 4.1%). Similar results were obtained for the products from reaction (IV).

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