*Reaction of Benzoyl Peroxide with Phenols Substituted with Electron-Withdrawing Groups**

By Hakuai INOUE, Osamu SIMAMURA and Kanichiro TAKAMIZAWA

(Received September 4, 1962)

Ever since benzoyl peroxide was recognized as a typical radical generator in solution[1], a great many investigations have been made to elucidate the nature of the reactions which ensue from the homolytic rupture of benzoyl peroxide in various solvents[2]. The detailed reaction pattern depends on the nature of a substrate compound in which benzoyl peroxide is allowed to decompose. Among other substrates phenols are of particular interest, since they act as efficient inhibitor or retarder of free-radical reactions, especially of autoxidation. Studies[3-6] carried out on the reaction with phenols show that the reaction of benzoyl peroxide takes place quite differently in phenols than in other solvents; a marked feature in phenols is that carbon dioxide is evolved in very much smaller amounts than in other solvents, and that the yield of benzoic acid is correspondingly higher, thus:

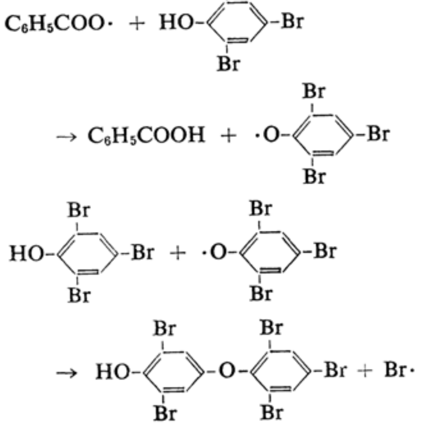
$$(C_6H_5COO)_2 \rightarrow 2C_6H_5COO\cdot$$

$$C_6H_5COO\cdot + ArOH \rightarrow C_6H_5COOH + ArO\cdot$$

The aryloxy radical ArO· produced from phenols by abstraction of a hydrogen atom of the hydroxyl group is comparatively stable because of the conjugation of the odd electron on the oxygen atom with the π-electron system of the nucleus and consequently tends to dimerize giving dihydroxybiphenyls rather than to attack some other molecules. The aryloxy radical may also cause, according to its reactivity, the induced decomposition of benzoyl peroxide giving a benzoyloxy derivative of the phenol and a benzoyloxy radical. Recently, on the basis of kinetic evidence, Walling and Hodgdon[7] have put forward a simple bimolecular "four-center" mechanism without radical formation for the reaction between benzoyl peroxide and phenols at 30°C.

Except for Walling and Hodgdon's work which included *m*-chloro-, *p*-chloro-, and *p*-bromo-phenol, previous studies have been carried out on phenol and phenols substituted with electron-releasing groups. We now report the results of a study on the reaction of benzoyl peroxide with various phenols with electron-withdrawing groups such as halogens and nitro group.

The Reaction of Benzoyl Peroxide with 2,4,6-Tribromophenol. — Benzoyl peroxide was refluxed with 2, 4, 6-tribromophenol in carbon tetrachloride and there were isolated as major products benzoic acid and a polymeric material of an approximate molecular weight of 3600∼4800, whose chemical constitution was shown to be polydibromophenylene oxide $H(OC_6H_2\cdot Br_2)_nBr$. Minor products are shown in Table I. In one experiment 2, 6-dibromo-4-(2, 4, 6-tribromophenoxy)-phenol ($n=2$ in the above formula) was isolated. The structure of this compound suggests the following mechanism in which a benzoyloxy radical generated by unimolecular decomposition of benzoyl peroxide abstracts a hydrogen atom from the hydroxy group of 2, 4, 6-tribromophenol and the resulting 2, 4, 6-tribromophenoxy radical then attacks 2, 4, 6-tribromophenol to give 2, 6-dibromo-4-(2, 4, 6-tribromophenoxy)phenol and a bromine atom.



(1)

(2)

---

* Most of the material of this paper was presented in parts at the 6th, the 7th, and the 9th Annual Meeting of the Chemical Society of Japan held in Kyoto in 1953, in Tokyo in 1954, and in Kyoto in 1956, respectively.

[1] D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

[2] For reviews see C. Walling, "Free Radicals in Solution", John Wiley & Sons, Inc., New York (1957), p. 474, and T. Suehiro, "Yukihannokiko no Simpo", Vol. 1, Maki Syoten, Tokyo (1958), p. 119.

[3] C. Walling, *J. Am. Chem Soc.*, **66**, 1602 (1944).

[4] P. D. Bartlett and K. Nozaki, ibid., **69**, 2299 (1947).

[5] S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, **1949**, 3189; **1951**, 388.

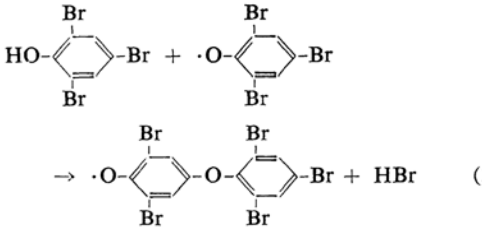
[6] T. Suehiro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 301 (1951).

[7] C. Walling and R. B. Hodgdon, *J. Am. Chem. Soc.*, **80**, 228 (1958).

TABLE I. REACTION OF BENZOYL PEROXIDE WITH 2, 4, 6-TRIBROMOPHENOL

	Reactant	mol.	Product	mol./mol. peroxide
(a)	$HOC_6H_2Br_3$	0.024~0.05	CO_2	0.1~0.26
	$(C_6H_5COO)_2$	0.015	Br_2	0.2~0.4
			C_6H_5COOH	1.7~1.8
	Refluxed 22 hr. in CCl_4 (40 cc.)		C_6H_6	trace
			C_6H_5Br	trace
			$H(C_6H_2Br_2O)_nBr$	(5~6.7 g.)
(b)	$HOC_6H_2Br_3$	0.276	CO_2	not measured
	$(C_6H_5COO)_2$	0.056	HBr	0.11
			Br_2	0.48
	Refluxed 17 hr. in CCl_4 (400 cc.)		C_6H_6	trace
			C_6H_5Br	0.1
			$(C_6H_5)_2$	trace
			C_6H_5COOH	1.89
			$C_6H_5COOC_6H_5$	0.002
			$H(C_6H_2Br_2O)_2Br$	0.14
			$H(C_6H_2Br_2O)_nBr$	(34 g.)
			$HOC_6H_2Br_3$ (recovered)	2.5

It may be plausible to suppose that in step 2 a 2, 6-dibromo-4-(2, 4, 6-tribromophenoxy)-phenoxy radical and hydrogen bromide are produced without liberation of any bromine atoms:



(3)

This view is supported by the fact that no chlorine was formed at all in the reaction of benzoyl peroxide with 2, 4, 6-trichlorophenol under similar experimental conditions.

The bromine atoms produced in step 2 may combine to give molecular bromine or react with phenols (ArOH), affording aryloxy radicals including 2, 4, 6-tribromophenoxy-, 2, 6-dibromo-4-(2,4,6-tribromophenoxy)phenoxy radicals etc.:

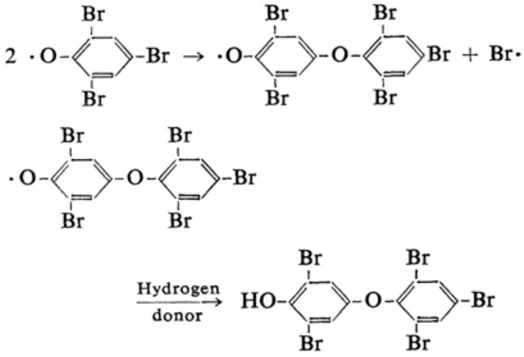
$$2Br\cdot \longrightarrow Br_2$$

$$Br\cdot + ArOH \rightleftharpoons HBr + ArO\cdot$$

Bromine can also be produced from hydrogen bromide by oxidation with benzoyl peroxide.

Obviously, successive attack by aryloxy radicals on phenols at a nuclear position carrying a bromine atom according to the above mechanism (step 2 or 3) leads to the formation of polymeric $H(OC_6H_2Br_2)_nBr$.

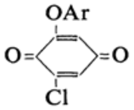
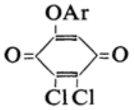
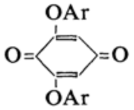
However, the possibility cannot be excluded that two of the tribromophenoxy radical react with each other with expulsion of a bromine atom giving a 2, 6-dibromo-4-(2, 4, 6-tribromophenoxy)phenoxy radical, which then affords a molecule of the corresponding phenol by abstracting an atom of hydrogen from a hydrogen donor, that is, presumably from another molecule of phenols or from a molecule of hydrogen bromide, one of the reaction products:



Continuation of such a reaction between two aryloxy radicals may similarly result in the formation of the polydibromophenylene oxide $H(OC_6H_2Br_2)_nBr$.

As for the minor products there scarcely seems to be any need of comments, since these are the usual products in the decomposition of benzoyl peroxide in solvents. Carbon dioxide was evolved in much larger amount than in the decomposition in phenol itself and in phenols with an electron-releasing group. This fact seems to indicate that the benzoyloxy radical has a little more difficulty in abstracting a hydrogen atom from tribromophenol.

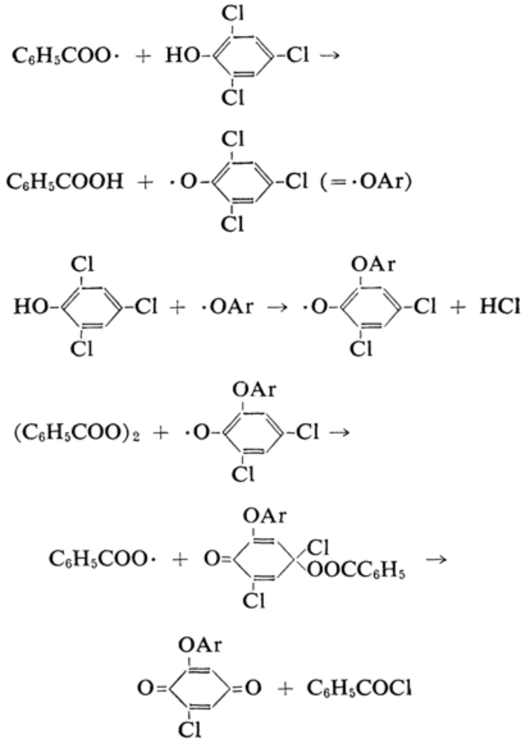
TABLE II. REACTION OF BENZOYL PEROXIDE WITH 2,4,6-TRICHLOROPHENOL

Reactant	mol.	Product	mol./mol. peroxide
$HOC_6H_2Cl_3$	0.426	C_6H_5COOH	0.60
$(C_6H_5COO)_2$	0.15	HCl	a large amount but not determined
		C_6H_6	0.04
Refluxed 30 hr. in CCl_4 (360 cc.)		C_6H_5Cl	0.087
		$HOC_6H_2Cl_2COOCH_3$	0.018
			0.002
			0.005
			0.0013
		C_6H_5COCl	0.113
		$HOC_6H_2Cl_3$ (recovered)	0.162

Ar=2,4,6-Trichlorophenyl

Hunter and his coworkers[8] had observed that in the presence of trace amount of bromine vapour potassium or silver 2,4,6-tribromophenoxide decomposes to give polydibromophenylene oxide. This fact indicates that bromine and tribromophenoxide can give tribromophenoxy radicals, which then start the chain reaction to give the polymeric material similarly to the case initiated by benzoyl peroxide. Recently Price[9] has reported the formation of polyphenylene oxides by oxidation of substituted *p*-bromophenols and proposed a mechanism involving the aryloxy radical.

The Reaction of Benzoyl Peroxide with 2, 4, 6-Trichlorophenol.—The results of the reaction of benzoyl peroxide with 2, 4, 6-trichlorophenol in boiling carbon tetrachloride are tabulated in Table II. Although a considerable amount of tar was formed, a polymeric material corresponding to polydibromophenylene oxide could not be isolated. Among other products, however, 2-chloro-6-(2, 4, 6-trichlorophenoxy)-, 2, 3-dichloro-6-(2, 4, 6-trichlorophenoxy)-, and 2, 6-bis-(2, 4, 6-trichlorophenoxy)-*p*-benzoquinone are worth mentioning. Obviously their isolation indicates the formation of 2, 4, 6-trichlorophenoxy radicals by attack of the benzoyloxy radical on 2, 4, 6-trichlorophenol. Further the formation of benzoyl chloride is remarkable, and a separate experiment showed that it is formed even in the absence of carbon tetrachloride as solvent. These findings immediately suggest the following steps for the mechanism of the formation of the quinones:



---

[8] W. H. Hunter, A. O. Olson and E. A. Daniels, *J. Am. Chem. Soc.*, 38, 1761 (1916); W A. Hunter and G. H. Woollett, ibid., 43, 135 (1921).

[9] G. D. Staffin and C. C. Price, ibid., 82, 3632 (1960); C. J. Kurian and C. C. Price, *J. Polymer Sci.*, 49, 267 (1961).

Table III. Products from reaction of 2,4,6-trichlorophenol (1.0 g.) with lead dioxide (7.0 g.)

Reactant	g.	Product, g.	In the Presence of 2,6-dichloro-*p*-benzoquinone (1.0 g.)	In the Absence of 2,6-dichloro-*p*-benzoquinone (1.0 g.)
PbO_2	7.0	2,6-Dichloroquinone	1.1	0.01
$HOC_6H_2Cl_3$	1.0	2-Chloro-6-(2,4,6-trichlorophenoxy)-*p*-benzoquinone	0.8	0.8
		2,6-Bis-(2,4,6-trichlorophenoxy)-*p*-benzoquinone	0.07	0.07

Table IV. Reaction of benzoyl peroxide with 2,6-dihalogenophenols

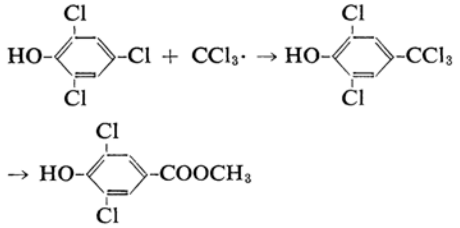
	Reactant,	mol.	Product	mol./mol. peroxide
(a)	$HOC_6H_3Cl_2$	0.1	C_6H_5COOH	1.13
	$(C_6H_5COO)_2$	0.05	$HOC_6H_2Cl_2C_6H_2Cl_2OH$	0.012
	Refluxed 20 hr. in CCl_4 (100 cc.)		C_6H_5COCl	detected
			HCl	detected
(b)	$HOC_6H_3Br_2$	0.074	C_6H_5COOH	1.72
			CO_2	0.13
	$(C_6H_5COO)_2$	0.021	$HOC_6H_2Br_2C_6H_2Br_2OH$	0.01
	Refluxed 25 hr. in CCl_4 (100 cc.)		Br_2	0.48
			$HOC_6H_2Br_3$	0.04
			$HOC_6H_3Br_2$ (recovered)	0.04

Similar steps will explain the formation of the other quinones. 2,3-Dichloro-6-(2,4,6-trichlorophenoxy)-*p*-benzoquinone seems to have been produced by chlorination of 2-chloro-6-(2,4,6-trichlorophenoxy)-*p*-benzoquinone, as is supported by an experiment described in the experimental part.

The isolation of methyl 3,5-dichloro-4-hydroxybenzoate suggests the involvement of trichloromethyl radicals derived from carbon tetrachloride, thus:

$$C_6H_5COO\cdot \rightarrow C_6H_5\cdot + CO_2$$

$$C_6H_5\cdot + CCl_4 \rightarrow C_6H_5Cl + CCl_3\cdot$$



Any substituted *o*-benzoquinones could not be isolated; such compounds would have decomposed under the present experimental conditions because of their instability. No chlorine was detected at all; since benzoyl peroxide does not oxidize hydrochloric acid to chlorine, this fact suggests that either the substitution of trichlorophenol by the trichlorophenoxy radical takes place without producing free chlorine atoms or these atoms, if produced at all, are very quick to abstract a hydroxyl hydrogen atom from the phenol.

Another mechanism for the production of aryloxyquinones from trichlorophenol is initial formation of 2,6-dichloro-*p*-benzoquinone followed by substitution of chlorine with 2,4,6-trichlorophenoxy radicals. The following findings, however, rule out this possibility. Since the same aryloxyquinones, viz., 2-chloro-6-(2,4,6-trichlorophenoxy)- and 2,6-bis-(2,4,6-trichlorophenoxy)-*p*-benzoquinone, are formed by oxidation of 2,4,6-trichlorophenol with lead dioxide at room temperature[10], it is reasonable to suppose that the same mechanism should be operative in the oxidation with lead dioxide as well as with benzoyl peroxide. In order to examine the effect of 2,6-dichloro-*p*-benzoquinone oxidation of 2,4,6-trichlorophenol with lead dioxide was carried out both in the presence and in absence of the dichloroquinone; the results tabulated in Table III show that the yield of aryloxyquinones were nearly equal in both experiments and that the dichloroquinone added beforehand was recovered unchanged, eliminating the formation of this compound as an intermediate.

The Reaction of Benzoyl Peroxide with 2,6-Dihalogenophenols.—The results of the reaction are summarized in Table IV. In the reaction with 2,6-dibromophenol bromine and 2,4,6-tribromophenol were formed, whereas hydrogen chloride and benzoyl chloride were detected in the reaction with 2,6-dichlorophenol. The formation of these products indicates that at

---

[10] W. H. Hunter and H. Morse, *J. Am. Chem. Soc.*, **48**, 1615 (1926).

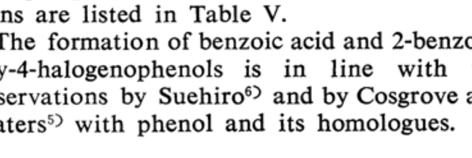
TABLE V. REACTIONS OF BENZOYL PEROXIDE WITH *p*-HALOGENOPHENOLS

	Reactant	mol.	Product	mol./mol. peroxide
(a)	*p*-ClC_6H_4OH	0.195	C_6H_5COOH	1.32
	$(C_6H_5COO)_2$	0.067	HCl	detected
	Refluxed 12.5 hr. in CCl_4 (100 cc.)		$ClC_6H_3(OH)OCOC_6H_5$	0.545
(b)	*p*-BrC_6H_4OH	0.302	C_6H_5COOH	1.45
	$(C_6H_5COO)_2$	0.1	$BrC_6H_3(OH)OCOC_6H_5$	0.284
	Refluxed 35.5 hr. in CCl_4 (100 cc.)		BrC_6H_4OH	0.121
(c)	*p*-IC_6H_4OH	0.08	C_6H_5COOH	0.94
	$(C_6H_5COO)_2$	0.039	$IC_6H_3(OH)OCOC_6H_5$	0.18
	Refluxed 13 hr. in CCl_4 (80 cc.)		I_2	0.24
			IC_6H_4OH	0.017

TABLE VI. REACTION OF BENZOYL PEROXIDE WITH NITROPHENOLS

	Reactant	mol.	Product	mol./mol. peroxide
(a)	*p*-$NO_2C_6H_4OH$	0.10	C_6H_5COCl	detected
	$(C_6H_5COO)_2$	0.05	HCl, CO_2	detected
	Refluxed 15 hr. in CCl_4 (400 cc.)		*p*-$NO_2C_6H_4OH$, (recovered)	2.0
(b)	*p*-$NO_2C_6H_4OH$	0.10	C_6H_5COOH	1.65
	$(C_6H_5COO)_2$	0.05	CO_2	0.22
	at 100°C		$C_6H_5COOC_6H_4NO_2$	trace
			$HOC_6H_4NO_2$, (recovered)	0.073
(c)	*o*-$NO_2C_6H_4OH$	0.20	CO_2	0.59
	$(C_6H_5COO)_2$	0.10	C_6H_5COOH	0.93
	at 100°C		4-$C_6H_5C_6H_4COOH$	0.02
			$HOC_6H_3(NO_2)C_6H_5$	0.11
			$C_6H_5COOC_6H_5$	0.019

least part of the reaction mechanism is essentially similar to that in the case of tribromo- or trichloro-phenol, although any substances containing a diphenyl ether linkage could not be isolated. In contrast to the case with trihalogenophenols 2,6-dibromophenol gave 3,5,3′,5′-tetrabromo-4,4′-dihydroxybiphenyl, and 2,6-dichlorophenol, the corresponding tetrachloro-compound. Evidently dimerization of the dihalogenophenoxy radical gave the tetrahalogenodihydroxybiphenyl:



The Reaction of Benzoyl Peroxide with *p*-Halogenophenols. — Products from these reactions are listed in Table V.

The formation of benzoic acid and 2-benzoyloxy-4-halogenophenols is in line with the observations by Suehiro⁶⁾ and by Cosgrove and Waters⁵⁾ with phenol and its homologues.

The Reaction of Benzoyl Peroxide with *o*- and *p*-Nitrophenols. — The results are shown in Table VI.

When a mixture of benzoyl peroxide and *p*-nitrophenol was refluxed in carbon tetrachloride, benzoyl peroxide reacted only with carbon tetrachloride and the whole of the *p*-nitrophenol used was recovered. However, when both components were allowed to react at 100°C in the absence of any solvent, an appreciable amount of carbon dioxide was evolved in contrast to the reactions with other phenols. The isolated products were *p*-nitrophenyl benzoate and benzoic acid.

Similarly, *o*-nitrophenol gave at 100°C carbon dioxide, benzoic acid, 4-biphenylcarboxylic acid, phenyl-*o*-nitrophenol, and phenyl benzoate. In this case phenylation of *o*-nitrophenol occurred; no such reaction has ever been observed with phenols. These results show that the benzoyloxy radical abstracts a hydrogen atom from nitrophenols only with difficulty and therefore has to decompose into carbon dioxide and a phenyl radical.

Experimental

Materials.—Benzoyl peroxide was recrystallized twice from chloroform and methanol, m. p. 106°C (decomp.), purity 99.8% as determined by iodometry. 2,4,6-Tribromophenol, prepared according to Vanino[11], had m. p. 96°C. 2,4,6-Trichlorophenol was prepared by chlorination of phenol with sodium hypochlorite solution[12], m. p. 66~67°C. 2,6-Dibromophenol was synthesized according to Huston and Neeley's method[13], m. p. 56°C. 2,6-Dichlorophenol was synthesized from *t*-butyl *p*-hydroxybenzoate by chlorination with sulphuryl chloride followed by hydrolysis and decarboxylation[14]. *p*-Chlorophenol was obtained from phenol and sulphuryl chloride[15], b. p. 99°C/11 mmHg, m. p. 44°C. *p*-Bromophenol was prepared by bromination of phenol in carbon disulphide[16], m. p. 64°C, b. p. 145~150°C/25 mmHg. *p*-Iodophenol was synthesized from *p*-aminophenol by diazotization followed by action of potassium iodide[17], m. p. 94°C. *o*- and *p*-Nitrophenols were prepared by nitration of phenol[18], m. p. 46.5~47.5° and 114°C, respectively.

Reaction of Benzoyl Peroxide with 2,4,6-Tribromophenol.—a) Benzoyl peroxide (3.63 g.) and 2,4,6-tribromophenol (8.00 g.) were heated in boiling carbon tetrachloride (40 cc.) for 22 hr., nitrogen being passed through the reaction mixture. The effluent nitrogen was passed through aqueous potassium hydroxide solution to determine the carbon dioxide formed. From the red-coloured reaction mixture carbon tetrachloride was distilled, and the bromine formed came over with it. The distillate, boiled with concentrated nitric acid and concentrated sulphuric acid, gave trace of *m*-dinitrobenzene indicating the formation of benzene. The residue from the distillation was extracted with aqueous sodium hydrogen carbonate solution, and the aqueous solution, on acidification, precipitated benzoic acid, which was then collected and weighed (2.23~2.36 g.). Then the residue was subjected to steam distillation to give tribromophenol. The resulting light brown residue was dissolved in chloroform, and addition of ethanol to the solution gave a precipitate. The precipitate was collected and dried to give white powder. This material is soluble in chloroform, ether, and benzene, but insoluble in methanol and petroleum ether, begins to soften at 240°C and melts at 260~285°C. It had molecular weight 3600~4800 (cryoscopy in bromoform or benzene) contained no benzoyloxy group, and strongly resisted hydrolysis in aqueous alkaline solution. The results of elemental analysis (Found: C, 26.75; H, 1.19; Br, 63.78, 64.05. Calcd. for $C_6H_2Br_2O$: C, 28.80; H, 0.80; Br, 64.00%) show that this compound must be a polymer consisting of many units of the dibromophenoxy group, $H(OC_6H_2Br_2)_nBr$. The same polymeric material was also obtained in the reaction in ligroin (b. p. 150°C).

b) Benzoyl peroxide (13.5 g.) was gradually added in small portions during 15 hr. to a boiling solution of 2,4,6-tribromophenol (91.5 g.) in carbon tetrachloride (400 cc.). After the addition of benzoyl peroxide was over, the solution was kept boiling for a further 15 hr. The gas evolved during the reaction was passed through a trap cooled with dry ice-ethanol, and then through acidic silver nitrate solution. The weight of the silver bromide precipitated gave the amount of hydrogen bromide formed (0.49 g.). The carbon tetrachloride was distilled from the reaction vessel and the bromine which came over with it was determined by the usual method (0.027 mol.). The carbon tetrachloride was treated with a mixture of nitric acid and sulphuric acid giving traces of dinitrobenzene. The residue was further distilled under reduced pressure (2 mmHg) and treatment of the distillate with a mixture of nitric acid and sulphuric acid gave 2,4-dinitrobromobenzene (1.14 g.). The residue was extracted with aqueous sodium carbonate and the extract acidified to pH 6 to give 2,4,6-tribromophenol (45.0 g.), which was filtered off. The filtrate, on acidification to Congo red, yielded benzoic acid (12.8 g.). The neutral residue was extracted with warm petroleum ether, giving polydibromophenylene oxide as insoluble part, and the extract was distilled in vacuo to yield phenyl benzoate (40 mg.) and a new compound (b. p. 200°C/5×10^{-4} mmHg) melting at 167~168°C (from methanol) (3.8 g.). This compound was identified with 2,4,6,3′,5′-pentabromo-4′-hydroxydiphenyl ether on the basis of molecular weight measurement (Found: 583 (Rast). Calcd. for $H(OC_6H_2Br_2)_2Br$: 581) and the results of the following debromination: In the presence of palladium-calcium carbonate catalyst in ethanol the compound absorbed five moles of hydrogen, affording the corresponding amount of bromide ions and one mole of *p*-hydroxydiphenyl ether, melting point and mixed melting point with an authentic specimen, 85°C. Incidentally another debromination by Raney alloy in aqueous alkaline solution brought about splitting of the ether linkage as well as debromination, and produced two molecules of phenol.

The Reaction of Benzoyl Peroxide with 2,4,6-Trichlorophenol.—Benzoyl peroxide (36.4 g.) was allowed to react with 2,4,6-trichlorophenol (85.0 g.) in boiling carbon tetrachloride for 30 hr. with purified nitrogen being passed. Evolution of hydrogen chloride was observed during the reaction. After the reaction was over, the solvent was removed by distillation on a water bath. The distillate, boiled with a mixture of concentrated nitric acid and concentrated sulphuric acid gave *m*-dinitrobenzene. The residue was further distilled at 170 mmHg to afford benzoyl chloride, which on hydrolysis gave 0.2 g. of benzoic acid, and chlorobenzene, which on nitration gave 2.65 g. of 2,4-dinitrochlorobenzene. The residue was extracted with methanol and the extract was distilled in steam to give trichlorophenol (32 g.), benzoic acid (11 g.), and methyl benzoate (2 g.). Vacuum distillation

---

[11] L. Vanino, "Handbuch der Präparativen Chemie", 3rd Ed., Ferdinand Enke, Stuttgart (1937), p. 432.

[12] W. H. Hunter and L. M. Seyfried, *J. Am. Chem. Soc.*, 43, 151 (1921).

[13] R. C. Huston and A. N. Neeley, ibid., 57, 2176 (1935).

[14] D. S. Tarbell, J. W. Wilson and P. E. Fanta, "Organic Syntheses", 29, 35 (1949).

[15] H. F. Fierz-David and L. Blangey, "Grundlegende Operationen der Farbenchemie", 4th Ed., Julius Springer, Wien (1938), p. 98.

[16] R. Adams and C. S. Marvel, "Organic Syntheses", Coll. Vol. I (1948), p. 128.

[17] F. B. Dains and F. Eberly, ibid., Coll. Vol. II (1950), p. 355.

[18] J. B. Fischman, *J. Am. Chem. Soc.*, 42, 2291 (1920).

of the residue gave methyl 3,5-dichloro-4-hydroxybenzoate (0.6 g.), m. p. 122°C (from petroleum ether) (Found: mol. wt., 198 (Rast); Cl, 31.63. Calcd. for $C_8H_6Cl_2O_3$: mol. wt., 221; Cl, 32.12%). The identification was done by hydrolyzing it with alkali to 3,5-dichloro-4-hydroxybenzoic acid, melting point and mixed melting point with an authentic specimen 256°C, and by converting the ester into the known acetyl derivative, m. p. 70∼71°C. When the residue from the vacuum distillation was dissolved in ether and the solution left to stand, 2,6-bis-(2,4,6-trichlorophenoxy)-*p*-benzoquinone (1.0 g.), m. p. 241∼243°C, mixed m. p. 240°C with authentic specimen[10], was obtained. Ether was removed from the filtrate and vacuum distillation at 10^{-3} mmHg of the residue gave 2-chloro-6-(2,4,6-trichlorophenoxy)-*p*-benzoquinone (0.1 g.), melting point and mixed melting point with an authentic specimen[10] 120.5∼121°C, and 2,3-dichloro-6-(2,4,6-trichlorophenoxy)-*p*-benzoquinone (2.79 g.), m. p. 155∼156°C (Found: mol. wt., 387 (Rast); Cl, 47.85. Calcd. for $C_{13}H_3O_3Cl_5$: mol. wt., 372; Cl, 47.64%). The structure of the latter quinone was established both by its preparation by chlorination of the former quinone with hydrochloric acid and potassium bichromate on a boiling water bath and by its conversion into 2,5-dianilino-6-chloro-*p*-benzoquinone, melting point and mixed melting point with an authentic specimen 263°C, and trichlorophenol on treatment with aniline and aniline hydrochloride on a boiling water bath.

The residual tarry material (mol. wt., 650 by cryoscopy in benzene) contained 47.0% of chlorine and 3.5% of the benzoyloxy group.

Reaction of Benzoyl Peroxide with 2,4,6-Trichlorophenol in the Absence of Solvent.—Benzoyl peroxide (12.2 g.) and 2,4,6-trichlorophenol (39.0 g.) were allowed to react in the absence of solvent at 100°C on a water bath for 20 hr. After the reaction was over, vacuum distillation (2 mmHg) gave benzoyl chloride in a trap which was cooled in dry ice-ethanol mixture, and it was characterized by the formation of benzanilide, m. p. and mixed m. p. 162°C.

Reaction of 2,4,6-Trichlorophenol with Lead Dioxide.—2,4,6-Trichlorophenol (1.0 g.) was allowed to react with lead dioxide (7.0 g.) in the presence of anhydrous sodium sulphate in benzene (40 cc.) with and without 2,6-dichloro-*p*-benzoquinone (1.0 g.) at room temperature for 30 hr. The lead dioxide was filtered off and extracted with benzene, the filtrate and the benzene extract were combined and distilled, and the residue was subjected to sublimation on a boiling water bath to give 2,6-dichloro-*p*-benzoquinone (1.1 g. in the reaction in the presence of 2,6-dichloro-*p*-benzoquinone; 0.1 g. in the absence of the quinone). When the residue from the sublimation was dissolved in small amount of ether, 2,6-bis-(2,4,6-trichlorophenoxy)-*p*-benzoquinone precipitated (0.07 g. each in both experiments), and the filtered ether solution gave on condensation 2-chloro-6-(2,4,6-trichlorophenoxy)-*p*-benzoquinone (0.8 g. each in both experiments).

The Reaction of Benzoyl Peroxide with 2,6-Dibromophenol. — Benzoyl peroxide (5 g.) was allowed to react with 2,6-dibromophenol (20.0 g.) in boiling carbon tetrachloride (100 cc.) for 25 hr., with purified nitrogen being passed. As in the case of tribromophenol, bromine (0.14 g.) was produced during the reaction, and the amount of carbon dioxide evolved was 0.12 g. Benzoic acid (4.3 g.) was obtained from the reaction mixture by extracting with aqueous sodium hydrogen carbonate. On distillation of the residue, 2,6-dibromophenol (10.1 g.) was recovered, and 2,4,6-tribromophenol (0.3 g.) and 3,5,3′,5′-tetrabromo-4,4′-dihydroxybiphenyl (0.2 g., m. p. and mixed m. p. 268°C) were isolated.

The Reaction of Benzoyl Peroxide with 2,6-Dichlorophenol.—Benzoyl peroxide (12.1 g.) was allowed to react with 2,6-dichlorophenol (16.3 g.) in boiling carbon tetrachloride (100 cc.) for 20 hr., during which period evolution of hydrogen chloride was observed. Extraction of the reaction mixture with aqueous sodium hydrogen carbonate followed by acidification gave benzoic acid (7.4 g.). The residue from distillation of the carbon tetrachloride solution was subjected to distillation in vacuo to give 2,6-dichlorophenol (6.0 g.). The distillation residue was dissolved in ether, and the solution extracted with dilute sodium hydroxide solution. On acidification of the extract 3,5,3′,5′-tetrachloro-4,4′-dihydroxybiphenyl (0.2 g.) was isolated, m. p. and mixed m. p. 234°C.

The Reaction of Benzoyl Peroxide with *p*-Chlorophenol.—Benzoyl peroxide (16.2 g.) and *p*-chlorophenol (25.0 g.) in carbon tetrachloride solution were boiled on a water bath for 12.5 hr. with purified nitrogen being passed. The effluent gas was passed through a trap cooled with dry ice-ethanol and then through potassium hydroxide solution. Weight increase of the alkali solution was 0.256 g. This value and the amount of chloride ions (0.22 g.) in the solution determined by argentometry show that only hydrogen chloride evolved and evolution of carbon dioxide was very slight. Benzoic acid (11.5 g.) was separated from the reaction mixture by extraction with aqueous sodium hydrogen carbonate, and carbon tetrachloride was removed by distillation. The crystalline residue was recrystallized from benzene to give 2-benzoyloxy-4-chlorophenol, m. p. 147.5∼149.5°C (Found: mol. wt., 253 (Rast); Cl, 14.05. Calcd. for $C_{13}H_9O_3Cl$: mol. wt., 249; Cl, 14.28%). Its structure was established by its preparation by chlorination of catechol monobenzoate with sulphuryl chloride.

The Reaction of Benzoyl Peroxide with *p*-Bromophenol.—Benzoyl peroxide (24.2 g.) and *p*-bromophenol (52.0 g.) in carbon tetrachloride were refluxed for 35.5 hr. with purified nitrogen being passed. No gas was evolved during the reaction. The solvent was distilled, and in the distillate no benzene could be detected. When benzoic acid (17.6 g.) and *p*-bromophenol (21.0 g.) were separated as before, the residue changed to crystalline solid, which recrystallized from benzene gave 2-benzoyloxy-4-bromophenol, m. p. 156∼157°C (Found: mol. wt., 308, 284 (Rast); Br, 27.18, 27.36. Calcd. for $C_{13}H_9O_3Br$: mol. wt., 293; Br, 27.30%). The structure of this compound was proved by mixed melting point determination with the bromocatechol monobenzoate which was prepared by bromination of catechol monobenzoate with bromine in glacial acetic acid.

The Reaction of Benzoyl Peroxide with *p*-Iodophenol.—Benzoyl peroxide (9.5 g.) and *p*-iodophenol (17.5 g.) were boiled in carbon tetrachloride for 13 hr. with purified nitrogen being passed. No gas was evolved, but iodine (2.38 g.) was liberated. Vacuum distillation of the reaction mixture gave benzoic acid (4.43 g.) and *p*-iodophenol (3.78 g.). The solid residue, recrystallized from methanol, gave a white crystalline compound, m. p. 165~169°C (Found: C, 45.86; H, 2.81. Calcd. for $C_{13}H_9O_3I$: C, 45.88; H, 2.65%), which was thought to be 2-benzoyloxy-4-iodophenol.

The Reaction of Benzoyl Peroxide with *p*-Nitrophenol. — Benzoyl peroxide (12.1 g.) and *p*-nitrophenol (13.8 g.) were refluxed in carbon tetrachloride solution (100 cc.) on a water bath for 15 hr. Vigorous evolution of hydrogen chloride was observed during the reaction. The solvent was removed and vacuum distillation of the residue gave benzoyl chloride and a crystalline residue, which, on recrystallization from water, gave almost all the original *p*-nitrophenol unchanged.

A mixture of powdered *p*-nitrophenol (13.8 g.) and powdered benzoyl peroxide (12.1 g.) was gently heated with stirring on a water bath with nitrogen being passed. At about 90°C, the mixture melted into a viscous fluid and the melt was kept at 100°C for 13 hr. with stirring. During that period 0.484 g. of carbon dioxide evolved. A small amount of carbon tetrachloride was added to the reaction mixture and the mixture was distilled. In the distillate benzene (25 mg.) was detected (as *m*-dinitrobenzene). Steam distillation of the residue gave benzoic acid (10 g.) and codistillation with purified ligroin (b. p. 100~165°/25 mmHg) yielded *p*-nitrophenol (10.1 g.). The residue was extracted with warm petroleum ether, the extract condensed and the residue recrystallized from benzene to give *p*-nitrophenyl benzoate (20 mg.).

The Reaction of Benzoyl Peroxide with *o*-Nitrophenol.—A mixture of *o*-nitrophenol (27.5 g.) and benzoyl peroxide (24.2 g.) was heated on a boiling water bath for 17 hr. with agitation with purified nitrogen being passed. Carbon dioxide (2.6 g.) was evolved. To the reaction mixture carbon tetrachloride was added and the mixture distilled. Nitration of the distillate gave *m*-dinitrobenzene (0.2 g.). Steam distillation of the residue yielded phenyl benzoate (0.66 g.), *o*-nitrophenol (17.3 g.), benzoic acid (11.2 g.) and a yellow crysalline compound (2.35 g.). This yellow compound, recrystallized from methanol, melted at 103~104.5°C (Found: C, 67.14; H, 4.63; N, 6.40. Calcd. for $C_{13}H_9NO_3$: C, 66.98; H, 4.19; N, 6.51%) and seems to be phenyl-*o*-nitrophenol. The residue, distilled in super-heated steam, gave 4-biphenylcarboxylic acid (0.37 g.), m. p. and mixed m. p. 219~221°C.

Summary

Benzoyl peroxide has been allowed to react with various halogenophenols in boiling carbon tetrachloride and the nature of the products has been examined.

2,4,6-Tribromophenol gave benzoic acid, polydibromophenylene oxide $H(OC_6H_2Br_2)_nBr$, 4-hydroxy-3,5,2′,4′,6′-pentabromodiphenyl ether, carbon dioxide and bromine, whereas in the case of 2, 4, 6-trichlorophenol the corresponding polymeric material could not be isolated, but *p*-benzoquinones substituted with chlorine and the 2, 4, 6-trichlorophenoxy group were formed. The reaction with 2, 6-dichloro- and 2, 6-dibromophenol gave a small amount of the corresponding 3, 5, 3′, 5′-tetrahalogeno-4, 4′-dihydroxybiphenyls, a type of product which were not obtained in the other cases. *p*-Halogenophenols yielded an appreciable amount of halogenocatechol monobenzoates.

p-Nitrophenol did not react with benzoyl peroxide in boiling carbon tetrachloride, but at 100°C in the absence of any solvent this phenol as well as the ortho isomer underwent reaction with evolution of considerable amount of carbon dioxide. These observations are discussed in terms of mechanisms involving free radicals.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo