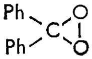
949. *Organic Peroxides. Part IV.*[1] *The Decomposition of Benzophenone Peroxide.*

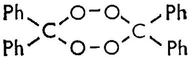
By J. I. G. Cadogan, D. H. Hey, and W. A. Sanderson.

The thermal decomposition of benzophenone peroxide in *p*-cymene and in nitrobenzene has been studied. In both cases the main reaction is elimination of oxygen to give benzophenone. In nitrobenzene, phenyl benzoate is also formed. The mode of formation of these products is discussed.

Lebedev *et al.*[2] ozonised 1,1,3,3-tetraphenylbut-1-ene and obtained a product which began to melt at 170° with the evolution of oxygen and the formation of benzophenone. They suggested that the compound was benzophenone peroxide and assigned the structure (I), although this was not supported by analysis or molecular-weight determination. Pure dimeric benzophenone peroxide (II) was first prepared by Kohler and Richtmyer[3] by the ozonisation of triphenylethylene, and these workers noted that it decomposed at 220—230° into benzophenone and oxygen. Since then, ozonisation of a number of compounds of the type $Ph_2C{:}CR'R''$ (R′, R″ = H, alkyl, or aryl) has been reported[4] to give dimeric benzophenone peroxide, m. p. 200—220°. Kambara, Okita, and Muto[5] also claim to have prepared the peroxide by the oxidation of thiobenzophenone and of benzophenone with hydrogen peroxide (30% w/w), but report m. p. 70°. Dilthey, Inkel, and Stephan[6] obtained phenyl benzoate (m. p. 70—71°) by this method, although acetone, cyclohexanone, and similar ketones gave the expected peroxides.

(I)

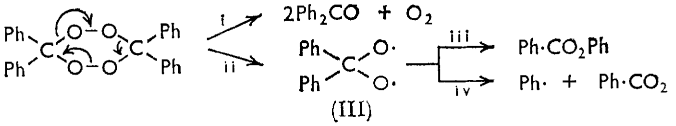




(II)

No work has been carried out to confirm the validity of the proposed cyclic structure (II) of dimeric benzophenone peroxide, but the observed molecular weight, together with the generally accepted cyclic structure of related peroxides,[7] suggests that the structure (II) is correct.

Although the thermal decomposition of the crystalline peroxide has been studied, no reports concerning its decomposition in solution have appeared. In theory, the decomposition can proceed by two ways: intramolecular elimination of oxygen to give benzophenone (reaction i), or homolysis of the peroxide links, either simultaneously or in succession, to give the diphenylmethylenedioxy-diradical (III) (reaction ii). Further breakdown of the diradical may then occur, again by two ways: rearrangement to give phenyl benzoate, or decomposition to give a phenyl radical and a benzoyloxy-radical, the latter in turn giving a further phenyl radical and carbon dioxide. Experiments designed to investigate these possibilities are now described. These involve the decomposition of the peroxide, prepared by the ozonisation of tetraphenylethylene, in *p*-cymene, which is an oxygen acceptor, and in nitrobenzene.



---

[1] Part III, Cadogan, Hey, and Sanderson, *J.*, 1960, 3203.
[2] Lebedev, Andreevsky, and Matyuschkina, *Ber.*, 1923, **56**, 2349.
[3] Kohler and Richtmyer, *J. Amer. Chem. Soc.*, 1930, **52**, 2038.
[4] Marvel and Nichols, (*a*) *J. Amer. Chem. Soc.*, 1938, **60**, 1455; (*b*) *J. Org. Chem.*, 1941, **6**, 296.
[5] Kambara, Okita, and Muto, *J. Chem. Soc. Japan*, 1949, **70**, 31.
[6] Dilthey, Inkel, and Stephan, *J. prakt. Chem.*, 1940, **154**, 219.
[7] Criegee, Schnorrenberg, and Hecke, *Annalen*, 1949, **565**, 7.

The results of these experiments, summarised in the Table, show that the main reaction is intramolecular decomposition of the peroxide to give benzophenone and oxygen (reaction i). Oxygen was not isolated as such but the reaction with *p*-cymene gave 4-methylacetophenone and *p*-isopropenyltoluene, both of which presumably arose by the thermal decomposition of α,α,4-trimethylbenzyl hydroperoxide formed by the oxidation of *p*-cymene, as in the annexed reaction scheme. The isolation in this case of 2,3-dimethyl-2,3-di-*p*-tolylbutane (IV), formed by dimerisation of the resonance-stabilised α,α,4-trimethylbenzyl radicals, is in accord with the reaction sequence given, which is also supported by the reported formation [8] of αα-dimethylbenzyl hydroperoxide in the analogous oxidation of isopropylbenzene. Foster and Williams [9] have moreover obtained the analogous α-methylstyrene on decomposition of benzoyl peroxide in isopropylbenzene in the presence of air, but not in the presence of nitrogen, indicating that α-methylstyrene was formed as a result of oxidation of the solvent. The amounts of 4-methylacetophenone, *p*-isopropenyltoluene, and 2,3-dimethyl-2,3-di-*p*-tolylbutane formed are consistent with the formulation given, but not all of the oxygen produced in the initial decomposition of the peroxide is accountable in this way. It is assumed that such an oxidation of *p*-cymene is an inefficient process.

$$\begin{aligned}
\mathrm{Ar{\cdot}CH(CH_3)_2} &\longrightarrow \mathrm{Ar{\cdot}C(CH_3)_2{\cdot}O{\cdot}OH} \longrightarrow \mathrm{Ar{\cdot}C(CH_3)_2{\cdot}O{\cdot}} + \mathrm{HO{\cdot}} \\
\mathrm{Ar{\cdot}C(CH_3)_2{\cdot}O{\cdot}} &\longrightarrow \mathrm{Ar{\cdot}CO{\cdot}CH_3} + \mathrm{{\cdot}CH_3} \\
\mathrm{Ar{\cdot}C(CH_3)_2{\cdot}O{\cdot}} + \mathrm{Ar{\cdot}CH(CH_3)_2} &\longrightarrow \mathrm{Ar{\cdot}C(CH_3)_2{\cdot}OH} + \mathrm{Ar{\cdot}\dot{C}(CH_3)_2} \\
\mathrm{Ar{\cdot}C(CH_3)_2{\cdot}OH} &\longrightarrow \mathrm{Ar{\cdot}C(CH_3){:}CH_2} + \mathrm{H_2O} \\
\mathrm{{\cdot}CH_3(or\ {\cdot}OH)} + \mathrm{Ar{\cdot}CH(CH_3)_2} &\longrightarrow \mathrm{CH_4(or\ H_2O)} + \mathrm{Ar{\cdot}\dot{C}(CH_3)_2} \\
\mathrm{2Ar{\cdot}\dot{C}(CH_3)_2} &\longrightarrow \mathrm{ArC(CH_3)_2{\cdot}C(CH_3)_2{\cdot}Ar}\ \mathrm{(IV)} \\
&\quad (\text{where Ar} = p\text{-}\mathrm{CH_3{\cdot}C_6H_4})
\end{aligned}$$

Decomposition of benzophenone peroxide in nitrobenzene and in p-*cymene*.*

Solvent	Temp.	Ph_2CO	$Ph{\cdot}CO_2Ph$	$Ph{\cdot}CO_2H$	Peroxide accounted for (%)
Nitrobenzene [1]	211°	1·47	0·23	0·29	94
p-Cymene [2]	176°	1·75	0	0·12	94

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

[1] Mean of two experiments; nitrobiphenyls (0·08 mole/mole) were also detected. [2] 4-Methylacetophenone (0·16 mole/mole), 2,3-dimethyl-2,3-di-*p*-tolylbutane (0·33 mole/mole), and *p*-isopropenyltoluene (0·25 mole/mole) were also formed.

No direct evidence for the formation of the diphenylmethylenedioxy-diradical (III) in the reaction with *p*-cymene is available, although small amounts if present would have escaped detection by our method of product analysis since they could be expected to give eventually some of the products (benzophenone, 2,3-dimethyl-2,3-di-*p*-tolylbutane) obtained by oxidation of the solvent. The isolation, on the other hand, of small quantities of phenyl benzoate from the reactions with nitrobenzene suggests the precursory formation, followed by rearrangement, of the diradical (III). Small amounts of benzoic acid were also extracted in these cases, but controlled extraction experiments showed that some, at least, of the acid was chemically bound in an unidentified alkali-labile compound other than phenyl benzoate or the nitrophenyl benzoates. In addition, infrared spectrographic analysis indicated that the experiments with nitrobenzene gave small amounts of nitrobiphenyls in proportions similar to those obtained by free-radical phenylation. Since benzophenone and phenyl benzoate are stable in these conditions, it is suggested that the decomposition of benzophenone peroxide in nitrobenzene also gives free phenyl radicals, possibly by way of the diradical (III).

---

[8] Hock and Lang, *Ber.*, 1944, **77**, 257; see also Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, 1951, **16**, 113.

[9] Foster and Williams, personal communication.

EXPERIMENTAL

Chromatographic separations were carried out on activated alumina (Peter Spence & Sons, Ltd., Type " H "). M. p.s were corrected. Gas–liquid chromatography was on 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 where possible by analysis of mixtures of known composition and found to be satisfactory.

Nitrobenzene (" AnalaR ") was purified as previously described.[10] *p*-Cymene was fractionally distilled under nitrogen. Analysis by gas–liquid chromatography showed no other components.

Dichlorodiphenylmethane (b. p. 126°/0·15 mm.) was prepared by the method of Staudinger and Freudenberger [11] who reported b. p. 180—181°/17 mm. Tetraphenylethylene (from benzene–ethanol), m. p. 230—234°, was prepared by the condensation of dichlorodiphenylmethane with diphenylmethane as described by Norris, Thomas, and Brown,[12] who reported m. p. 220—222°.

p-Isopropenyltoluene (b. p. 98°/30 mm., n_D^{22} 1·5340) was prepared by the dehydration (acetic anhydride) of α,α,4-trimethylbenzyl alcohol prepared from methylmagnesium iodide and 4-methylacetophenone. Bachmann and Hellman [13] reported b. p. 77°/19 mm., n_D^{25} 1·5290.

Dr. G. H. Williams of King's College, London, is thanked for a sample of 2,3-dimethyl-2,3-di-*p*-tolylbutane, m. p. 157—158°.

Benzophenone Peroxide.—The method of preparation was based on that of Marvel and Nichols.[4b] Ozonised oxygen (18 l./hr.; 1% of ozone) was passed for 3 hr. into a solution of tetraphenylethylene (2 g.) in carbon tetrachloride (125 ml.). The cloudy solution was filtered and the solvent was removed under reduced pressure. The residue, in ethanol (10 ml.) was filtered, to leave benzophenone peroxide (0·7 g., 58%), which, crystallised from dimethylformamide, had m. p. 216—217° (decomp.). Some variation in the m. p. was observed, according to crystal size and rate of heating [Found: C, 78·8; H, 5·15; *M* (ebullioscopic in benzene), 427. Calc. for $C_{26}H_{20}O_4$: C, 78·8; H, 5·1%; *M*, 396]. Marvel and Nichols [4] reported m. p. 206·5—215·5°, according to crystal size and rate of heating. The infrared spectrum showed the characteristic " peroxide " peak at 10·13 μ. The ethanolic filtrates, on evaporation, left a mixture of benzophenone and phenyl benzoate.

Attempts to prepare the peroxide by the reaction of (85% w/w) hydrogen peroxide with benzophenone or dichlorodiphenylmethane were unsuccessful. The former reaction gave an unidentified peroxide, m. p. 90—92°, which liberated iodine from acidified potassium iodide. The latter, which was very vigorous, gave benzophenone, m. p. and mixed m. p. 47—48°.

Decomposition of Benzophenone Peroxide in p-*Cymene.*—The peroxide (1·2900 g.) in *p*-cymene (100 ml.) was boiled under reflux (176°) in an atmosphere of nitrogen for 64 hr. The mixture was fractionally distilled under nitrogen through a helix-packed column (25 cm.) fitted with a suitable head. Analysis by gas–liquid chromatography of the first portion (12·5 g.) of the distillate showed that no benzene (<0·1%) was present. Extraction of the residue with saturated sodium hydrogen carbonate solution gave benzoic acid (0·0216 g.), m. p. and mixed m. p. 117—120° (from light petroleum). Extraction with 4N-sodium hydroxide gave more benzoic acid (0·0269 g.), m. p. and mixed m. p. 116—117°. The dried ($MgSO_4$) *p*-cymene solution was then distilled under nitrogen to leave a residue (*ca.* 10 ml.) which, on distillation at 0·1 mm., gave the following fractions: (*a*) b. p. <50° (8·682 g.); (*b*) b. p. 50—80° (1·613 g.); (*c*) b. p. 80—140° (1·5862 g.); a residue (0·0164 g.), b. p. >220°. Fraction (*a*) was shown by gas–liquid chromatography to be pure *p*-cymene. The infrared spectrum of fraction (*b*) indicated the presence of 4-methylacetophenone and *p*-cymene. It decolorised bromine water much more rapidly than a synthetic mixture of *p*-cymene and 4-methylacetophenone. It was analysed by gas–liquid chromatography through a 2-m. Perkin–Elmer " C " column (Dow Corning silicone oil D.C. 200/50c. S.T. on " Celite ") at 170°, with a column pressure 0·5 kg./cm.², nitrogen flow at 4 ml./min., and detector voltage at 6 v; this showed, by comparison with synthetic mixtures, that it contained *p*-cymene 88·9%, *p*-isopropenyltoluene 6·7%, and 4-methylacetophenone 4·4%. The retention times of these components, relative to *p*-cymene,

---

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

[11] Staudinger and Freudenberger, *Org. Synth.*, Coll. Vol. II, 573.

[12] Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2940.

[13] Bachmann and Hellman, *J. Amer. Chem. Soc.*, 1948, **70**, 1772.

were 1 : 1·3 : 1·8. The presence of 4-methylacetophenone was confirmed by condensing the vapour of the final fraction on a rock-salt plate, and recording the infrared spectrum, which corresponded to that of pure 4-methylacetophenone.

Fraction (*c*) could not be resolved by gas–liquid chromatography, even at 300°. A portion (0·7202 g.) of the homogenised fraction was chromatographed on alumina: elution with light petroleum (b. p. 60—80°) gave 2,3-dimethyl-2,3-di-*p*-tolylbutane (0·1316 g.), m. p. and mixed m. p. 156—158°; elution with benzene–light petroleum (b. p. 60—80°) (1 : 2) gave unidentified colourless crystals (0·0132 g.); elution with benzene gave benzophenone (0·4698 g.), m. p. and mixed m. p. 46—48°; elution with chloroform gave an unidentified yellow oil (0·0542 g.) which exhibited a strong infrared peak at 3 μ (OH); elution with methanol gave an unidentified yellow semisolid material (0·0201 g.), whose spectrum, although different from that of the preceding fraction, also showed a peak at 3 μ. The recovery from the column was 96%.

A control experiment, in which *p*-cymene alone was boiled under reflux under nitrogen for 64 hr., was worked up in the same way. Neither 4-methylacetophenone nor *p*-isopropenyltoluene was detected.

Decomposition of Benzophenone Peroxide in Nitrobenzene.—The peroxide (1·0936 g.) in nitrobenzene (170 ml.) was boiled under reflux for 6½ hr. The dark solution was extracted with saturated aqueous sodium hydrogen carbonate (3 × 75 ml.) and then with water (50 ml.). The combined aqueous portions were washed with benzene (30 ml.), which was added to the nitrobenzene portion, and were acidified. Extraction with ether (4 × 30 ml.) gave impure benzoic acid (0·0378 g.) (identified by infrared spectroscopy). Extraction of the nitrobenzene–benzene solution with 4N-sodium hydroxide (3 × 30 ml.) similarly gave more impure benzoic acid (0·1914 g.). Sublimation of the impure products gave benzoic acid (0·140 g.; m. p. and mixed m. p. 113—115°). The residue was not identified. Extraction of the nitrobenzene–benzene solution with 4N-hydrochloric acid (3 × 30 ml.) gave no product. The nitrobenzene–benzene solution was dried (Na_2SO_4) and distilled to leave a small residue, which was distilled to give a yellow oil (0·8576 g.; b. p. 82—92°/0·07 mm.) and a residue (0·0026 g.). The infrared spectrum of the oil indicated the presence of much benzophenone, together with phenyl benzoate and a small quantity of nitrobiphenyls (peaks at 6·53, 7·40, and 11·75 μ). The distillate, analysed by an infrared method making use of the carbonyl absorptions at 5·69 (phenyl benzoate) and 5·97 μ (benzophenone), contained benzophenone (79%) and phenyl benzoate (18·6%). A synthetic mixture of benzophenone (74·5%), phenyl benzoate (22·0%), and a mixture of isomeric nitrobiphenyls (3·5%), obtained by the phenylation of nitrobenzene with benzoyl peroxide, gave the following results on analysis by the same method: benzophenone, 72%; phenyl benzoate, 21·5%. The spectra of the synthetic and of the experimental mixtures were very similar, although it was evident that the latter contained more benzophenone and less ester.

The concentrations of nitrobiphenyls appeared to be approximately the same in each case. The mixture was not resolved by gas–liquid chromatography.

A portion (0·59 g.) of the homogenised product was chromatographed on neutralised, deactivated alumina, prepared by the method of Farrar, Hamlet, Henbest, and Jones.[14] Elution with light petroleum (b. p. 60—80°) (50 ml.) gave impure phenyl benzoate (0·044 g.). After recrystallisation from aqueous ethanol it had m. p. and mixed m. p. 67—70°. Further elution (600 ml.) gave a mixture (0·51 g.) of benzophenone and phenyl benzoate (infrared) and the final eluate (400 ml.) gave benzophenone (0·015 g.), m. p. and mixed m. p. 46—48°. The recovery from the column was 96%.

Chromatography on un-neutralised, activated alumina caused hydrolysis of phenyl benzoate.

Extraction Experiments.—It was shown that benzoic acid was extracted quantitatively from nitrobenzene solution by sodium hydrogen carbonate solution as described in the previous experiment, whereas phenyl benzoate and the isomeric nitrophenyl benzoates in nitrobenzene were not hydrolysed by sodium hydrogen carbonate or 4N-sodium hydroxide. Phenyl benzoate and benzophenone were shown to be stable in boiling nitrobenzene.

This work was carried out during the tenure (by W. A. S.) of a Peter Spence Fellowship. Thanks are accorded to Mr. G. Scott of Imperial Chemical Industries Limited for his help with the ozonisation experiments.

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

[*Received, April* 19*th*, 1960.]

---

[14] Farrar, Hamlet, Henbest, and Jones, *J.*, 1952, 2657.