

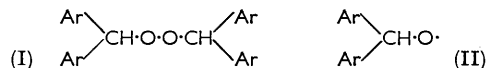
908. *Organic Peroxides. Part II.* The Decomposition of Bisdiphenylmethyl Peroxide.*

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Bisdiphenylmethyl peroxide has been prepared and its thermal decomposition in organic solvents studied. The reactions in bromobenzene, isopropylbenzene, and nitrobenzene are homolytic and give mainly benzophenone. In nitrobenzene at 210°, but not at 115°, phenyl radicals (0.03 mole/mole of peroxide) are also formed. The peroxide decomposes in ethanolic sodium ethoxide and in pyridine to give benzophenone and diphenylmethanol, probably by heterolysis.

SECONDARY aliphatic peroxides, where the substituent groups are aromatic, have received little attention. Davies *et al.*,¹ in an attempt to prepare di-*p*-methoxyphenylmethyl hydroperoxide, produced bis(di-*p*-methoxyphenylmethyl) peroxide (I; Ar = *p*-MeO·C₆H₄), but their method was not of general application. Earlier, Nauta² and his co-workers claimed to have isolated bis(di-2:4-dimethylphenylmethyl) peroxide and its 3:5-isomer from the reaction of the corresponding diphenylmethyl chloride with silver in the presence of oxygen. The yields were low, however, and the products were impure.

The preparation and decomposition of the hitherto unknown bisdiphenylmethyl peroxide (I; Ar = Ph) are now described. Attempts to prepare it by the condensation of diphenylmethyl hydroperoxide with diphenylmethanol (benzhydrol) in the presence of



toluene-*p*-sulphonic acid, by the method described by Hey, Stirling, and Williams³ for the preparation of tertiary peroxides, gave low yields of the peroxide contaminated by much bisdiphenylmethyl ether. The similarity in the melting points of the peroxide and the ether (112—113° and 110—111° respectively) and in their solubilities precluded a satisfactory separation, although small quantities of bisdiphenylmethyl peroxide were isolated after tedious fractional crystallisation. Further, it was found that appreciable amounts of bisdiphenylmethyl ether could be present in a sample of the peroxide without producing a large change in melting point. This, coupled with the incomplete reaction of the peroxide with acid potassium iodide, made it difficult to assess the purity of the product. This difficulty was overcome by the use of an infrared spectrographic method of analysis based on a strong absorption band (9.5 μ) in the spectrum of bisdiphenylmethyl ether which was absent from that of the peroxide. By this means it was found that the condensation of diphenylmethanol with diphenylmethyl hydroperoxide, when carried out in acetic acid, gave almost pure bisdiphenylmethyl peroxide.

* Part I, *J.*, 1957, 1054.

¹ Davies, Foster, and White, *J.*, 1954, 2200.

² Nauta, Ernsting, and Faber, *Rec. Trav. chim.*, 1941, **60**, 915; Nauta and Wuis, *ibid.*, 1938, **57**, 41.

³ Hey, Stirling, and Williams, *J.*, 1957, 1054.

By analogy with the decomposition of related peroxides⁴ it would be expected that bisdiphenylmethyl peroxide would give the radical (II; Ar = Ph) on thermal decomposition in solution. In theory, this radical can break down in two ways: (a) by elimination of a hydrogen atom with the formation of benzophenone, or (b) by the elimination of a phenyl radical with the formation of benzaldehyde. Our experiments were designed to distinguish between these possibilities.

Bisdiphenylmethyl peroxide was allowed to decompose in bromobenzene, isopropylbenzene, and nitrobenzene at various temperatures. The results are summarised in Table I, in which the figures, unless otherwise stated, refer to moles/mole of peroxide.

TABLE I.

Solvent	PhNO ₂			PhPr		PhBr- <i>p</i> -benzoquinone
Expt. No.	1 *	2	3 †	4 ‡	5 ‡	6 §
Peroxide (mmoles)	27.3	8.2	6.8	6.8	6.8	16.6
Temp.	210°	115°	152°	115°	115°	157°
Time (days)	(24 hr.)	7	7	7	7	137 (hr.)
Vol. of solvent (ml.)	400	120	100	100	100	200
Ph ₂ CO	1.48	1.69	1.40	1.57	1.60	1.40
Ph ₂ CH·OH	0.03	0.08	0.48	0.30	0.28	—
Di- α -cumyl	—	—	0.18	0.12	0.12	—
Peroxide accounted for (%)	75	88	97	94	94	70

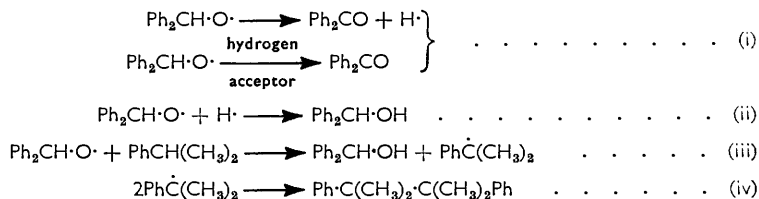
* Nitrodiphenyls (0.03 mole/mole) were formed.

† Ph₂CH·O·CHPh₂ (0.026 mole/mole) was formed.

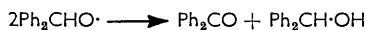
‡ Reactions carried out under N₂ in the dark.

§ Quinhydrone (0.58 mole/mole) was formed.

It is considered that decompositions in these solvents proceed by the initial production of a diphenylmethoxy-radical (II; Ar = Ph) which either loses a hydrogen atom to give benzophenone, or reacts by combination with another hydrogen atom, either free or bound, as in isopropylbenzene, to give diphenylmethanol:



The formation of di- α -cumyl (iv) is taken as proof that free radicals are involved in the reaction. It is significant that the amount of di- α -cumyl (2 : 3-dimethyl-2 : 3-diphenylbutane) produced does not exceed the amount of diphenylmethanol formed. It seems unlikely, therefore, that hydrogen atoms abstract hydrogen from cumene, to give cumyl radicals, in this reaction. The formation of a small amount of aniline in the experiment with nitrobenzene, and the formation of quinhydrone in the reaction in bromobenzene in the presence of *p*-benzoquinone, affords strong support for reactions (i). These results do not, however, enable us to decide whether hydrogen atoms are involved, or whether benzophenone is produced by bimolecular reaction of the radical Ph₂CHO· with a hydrogen acceptor (nitrobenzene or *p*-benzoquinone⁵). On the other hand, the formation of benzophenone in the reaction in cumene can hardly be explained on the basis of a bimolecular reaction, because cumene would be expected to donate, as in reaction (iii), rather than to accept a hydrogen atom. The other possible hydrogen acceptor present is the diphenylmethoxy-radical itself:



⁴ Hawkins, *Quart. Rev.*, 1950, **4**, 251.

⁵ Horeld and Huisgen, *Annalen*, 1949, **562**, 137.

but this formulation is inconsistent with the stoichiometry of the reaction, since, in all cases, the amount of benzophenone isolated is far in excess of the amount of diphenylmethanol formed. Indeed, appreciable amounts of diphenylmethanol were formed only in the experiments with cumene, and can be readily explained by invoking reaction (iii).

Only in one instance, that of the decomposition in nitrobenzene at the higher temperature (210°), was any evidence found for the formation of phenyl radicals. Chromatography of the products gave a fraction which was shown by infrared spectrography to consist of benzophenone with a mixture of nitrodiphenyls, of the same composition as that produced in the free-radical phenylation of nitrobenzene. This is the first recorded instance of the formation of a phenyl radical from the decomposition of an aliphatic peroxide.

The reluctance with which a phenyl radical is produced from the radical (II; Ar = Ph) is in agreement with observations on the decomposition of related peroxides and with Kharasch, Fono, and Nudenberg's⁶ statement that the relative tendency of groups R, R', or R'' in the radical RR'R''C·O to participate in cleavage of the R-C bond increases in the order Ph, Me, Et, H.

Bisdiphenylmethyl peroxide was also allowed to decompose in pyridine at 115°. In contrast to the above reactions, inconsistent results were repeatedly obtained, as indicated in Table 2.

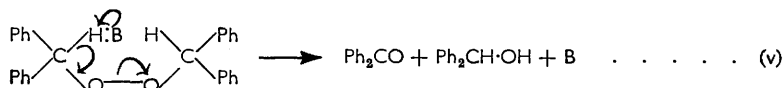
TABLE 2. *Decomposition of bisdiphenylmethyl peroxide in pyridine at 115°.*

Expt. No.	Time (days)	Ph ₂ CO	Ph ₂ CH-OH (Ph ₂ CH) ₂ O (moles/mole of peroxide)			Ph ₂ CO	Ph ₂ CH-OH	Recovery (%)
			Ph ₂ CH-OH	Ph ₂ CH-OH	Ph ₂ CH-OH	Ph ₂ CH-OH	Ph ₂ CH-OH	
7	3-5	0.95	0.89	0	1.07	1.07	92	
8	4	1.51	0.42	0	3.6	3.6	97	
9	7	0.97	0.92	0	1.05	1.05	95	
10	7	1.03	0.58	0.104	1.78	1.30	91	
11	10	0.99	0.80	0.083	1.24	1.02	97	
12 †	3	0.97	0.80	0.065	1.21	1.04	95	
13 †	3	0.98	0.94	0	1.04	1.04	96	

* *I.e.*, by assuming (Ph₂CH)₂O to be derived from Ph₂CH-OH.

† Reactions carried out under nitrogen in the dark.

It is believed that the main reaction is a base-catalysed decomposition of the peroxide producing equivalent amounts of benzophenone and diphenylmethanol, as observed in experiments 7, 9, and 13. The results of experiment 8 could be rationalised by assuming an initial reaction as in (v) followed by conversion of some diphenylmethanol into benzophenone, while the formation of bisdiphenylmethyl ether (expts. 10, 11, and 12) could be



explained by self-condensation of diphenylmethanol. A supplementary experiment involving pyridine and diphenylmethanol, in which very small amounts of the ether and benzophenone were formed, indicated however that these explanations are unsatisfactory. Although rigorously purified materials were used in the experiments it is difficult to explain the inconsistencies beyond invoking catalysis by traces of impurities. That the reaction in pyridine is heterolytic is supported by the results of a similar experiment in 2 : 6-lutidine. The products were benzophenone and diphenylmethanol, and no trace of any compound resulting from free-radical attack on the side chains was isolated or detected.

The decomposition of the peroxide in ethanolic sodium ethoxide gave benzophenone (0.27 mole/mole) and diphenylmethanol (1.58 moles/mole). A control experiment showed that under these conditions benzophenone is converted into diphenylmethanol in sufficient quantity to suggest that the initial reaction of the peroxide with sodium ethoxide is also

⁶ Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, 1950, **15**, 763.

of type (v), producing equivalent amounts of benzophenone and diphenylmethanol. The above reduction of benzophenone closely parallels the well-known reaction in propan-2-ol, when benzpinacol (1 : 2-diphenylethanediol) is first produced and then reduced to diphenylmethanol.⁷

Chromatography on alumina of a benzene solution of the peroxide gave an equimolar mixture of benzophenone and diphenylmethanol, thus providing a third example of base-catalysed decomposition.

EXPERIMENTAL

Chromatographic separations were carried out on activated alumina (Peter Spence & Sons, Ltd., Type "H").

Solvents.—Nitrobenzene ("AnalaR") was washed with aqueous sodium hydroxide (25%) until the washings were colourless, steam distilled, dried (CaCl₂), fractionally distilled through a 120 cm. helix-packed column, and finally fractionally frozen (3 times). Pyridine ("AnalaR") was dried (KOH) and fractionally distilled (120 cm. column) from barium monoxide. *iso*Propylbenzene was washed with sulphuric acid (*d* 1.8) until the washings were colourless, then with aqueous sodium hydrogen carbonate. After being dried (CaCl₂), the solvent was fractionally distilled (120 cm. column). The product was passed through an alumina column to remove hydroperoxide immediately before use. Bromobenzene was washed with aqueous sodium hydroxide (7*N*; 3 times), dried (Na₂SO₄), and fractionally distilled (120 cm. column). Bisdiphenylmethyl ether,⁸ recrystallised from chloroform-ethanol, had m. p. 110—111°.

Diphenylmethyl hydroperoxide was prepared by a modification of the method of Davies, Foster, and White.⁹ To hydrogen peroxide (86% w/w; 25 ml.; 6.3 mol.), sulphuric acid (*d* 1.8; 0.10 ml.), and ether (20 ml.), was added diphenylmethanol (30 g.; 0.16 mol.; m. p. 66°, Hopkin and Williams reagent crystallised from light petroleum, b. p. 60—80° in ether (15 ml.). The mixture was stirred magnetically for 6 hr. at room temperature. The usual precautions against explosion were taken. Water (50 ml.) was added, the mixture was separated, and the aqueous layer was extracted with ether (3 × 20 ml.). The ether solution was washed with sodium hydrogen carbonate solution and with water, and was dried (Na₂SO₄). Evaporation of the solution left the crude hydroperoxide (30 g.; 92%; m. p. 40—45°). Recrystallisation from light petroleum (b. p. 60—80°) gave diphenylmethyl hydroperoxide as colourless needles, m. p. 48—50°. Davies *et al.*⁹ report m. p. 50—52°.

Bisdiphenylmethyl Peroxide.—Attempts to prepare the peroxide, based on the general method described by the Hercules Powder Co.,¹⁰ from diphenylmethanol (excess of 1 mol.) and diphenylmethyl hydroperoxide (1 mol.) in the presence of toluene-*p*-sulphonic acid (catalytic quantity) under various conditions of time and temperature, gave mixtures of bisdiphenylmethyl ether and bisdiphenylmethyl peroxide which could not be satisfactorily resolved. Traces of the ether mixed with the peroxide were detected by infrared spectrography as described above. The following method of preparation was found to be satisfactory: Diphenylmethanol (5 g.), diphenylmethyl hydroperoxide (5 g.), toluene-*p*-sulphonic acid (0.026 g.), and acetic acid (15 ml.) were kept at 80° for 1 hr. Ethanol (60 ml.) was added and the mixture was cooled and kept at 0° for 1 hr. The product (3.7 g.; m. p. 110—112°) was filtered off and washed with light petroleum (b. p. 60—80°). Recrystallisation from chloroform-ethanol gave *bisdiphenylmethyl peroxide* as colourless needles, m. p. 112—113° (Found: C, 85.1; H, 6.0. C₂₆H₂₂O₂ requires C, 85.2; H, 6.1%). The purity of the diphenylmethanol was a critical factor in this preparation, traces of impurities presumably being able to catalyse the formation of bisdiphenylmethyl ether.

Decomposition of Bisdiphenylmethyl Peroxide in Nitrobenzene (Table 1).—(a) At 210°. The peroxide (10.00 g.) in nitrobenzene (400 ml.) was boiled under reflux for 24 hr. The solution, which had become dark red after 30 min., was extracted with sodium hydroxide (7*N*; 4 × 50 ml.) and with water. The aqueous extracts on being worked up for acid gave a black, unidentified oil (1.063 g.). The nitrobenzene solution was then extracted with hydrochloric acid (4*N*; 4 × 50 ml.) and then with water. Working-up of the aqueous portion gave

⁷ Finar, "Organic Chemistry," Longmans, London, 1951, p. 541.

⁸ Ward, *J.*, 1927, 2285.

⁹ Davies, Foster, and White, *J.*, 1953, 1541.

¹⁰ Hercules Powder Co., U.S.P. 2,668,180.

a basic oil (0.096 g.), which was shown to be aniline by the formation of benzeneazo- β -naphthol, m. p. and mixed m. p. 129°.

The nitrobenzene solution was reduced to 70 ml. by distillation through a 10 in. helix-packed column, and filtered through an alumina column, followed by elution with benzene (100 ml.) and ether (150 ml.). The mixed solvents were then distilled off (10 in. column). The residue was distilled to give an orange liquid (8.124 g.; b. p. 100—150°/0.4 mm.) and a residue (0.102 g.). Redistillation gave two fractions: (i) 7.865 g.; b. p. 98—120°/0.4 mm.; (ii) 0.249 g.; b. p. 128—160°/0.4 mm. Fraction (i) solidified when seeded with a crystal of benzophenone. A portion (1.179 g.) of homogenised fraction (i) on chromatography, and elution with benzene followed by ethanol, gave an orange semi-solid fraction (0.329 g.) followed by benzophenone (0.796 g.) and diphenylmethanol (0.022 g.), whose identities were established by mixed m. p.s and infrared spectra. The infrared spectrum of the first fraction from the chromatography indicated that it was largely benzophenone. The extra peaks in the spectrum corresponded to those of a mixture of nitrodiphenyls of the same isomeric composition as that produced by the decomposition of benzoyl peroxide in nitrobenzene. Comparison of the spectrum of the first fraction with those of mixtures of benzophenone and isomeric nitrodiphenyls of known composition confirmed the composition of the fraction, and established that the diaryls were present to the extent of 2% by weight of the first distillate.

Fraction (ii), on recrystallisation from chloroform-ethanol, gave a pale yellow solid, m. p. 148—153° (Found: C, 58.2; H, 3.9%), which could not be identified.

(b) At 115°. The above experiment was repeated in a thermostat. The results were qualitatively the same, with the exception that no nitrodiphenyls were detected.

Decomposition of Bisdiphenylmethyl Peroxide in isoPropylbenzene.—The peroxide (2.502 g.) was boiled under reflux in *isopropylbenzene* (100 ml.) for 7 days. The reaction mixture was extracted with sodium hydroxide (4N; 3 \times 25 ml.) and with water (1 \times 25 ml.). The aqueous extracts were washed with benzene (1 \times 25 ml.) which was combined with the cumene solution. The aqueous layer was worked up for acid content, but contained only a trace. The organic solution was distilled at atmospheric pressure (10 in. column) leaving a residual oil which was distilled to give the following fractions: (i) 0.042 g., b. p. <85°/0.1 mm.; (ii) 2.808 g., b. p. 85—125°/0.1 mm., and a residue (0.004 g.). Fraction (i) was acetophenone [2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 250°) and infrared spectrum]. Fraction (ii) was redistilled to give (iii) a colourless oil, 2.744 g., b. p. 94°/1 mm., (iv) a yellow solid, 0.061 g., b. p. 87—118°/0.05—0.1 mm., and a residue (0.001 g.). Fraction (iv) was bisdiphenylmethyl ether (m. p. and mixed m. p. 108°, infrared spectrum). Fraction (iii) was investigated as follows: a portion (1.371 g.) was dissolved in nitromethane (1 ml.) and cooled to -5°. The precipitated solid (0.077 g.) which was collected, washed with nitromethane and dried, had m. p. 115—117°, undepressed on admixture with 2 : 3-dimethyl-2 : 3-diphenylbutane (di- α -cumyl). The nitromethane filtrate and washings were evaporated and the residue was chromatographed. Elution with light petroleum (b. p. 40—60°) gave di- α -cumyl (0.07 g., m. p. and mixed m. p. 110—112°). Elution with light petroleum (b. p. 60—80°) and benzene gave benzophenone (0.872 g., m. p. and mixed m. p. 47°), and with ethanol gave diphenylmethanol (0.304 g., m. p. and mixed m. p. 64°).

The presence of acetophenone indicated that decomposition of cumene, by way of α -cumyl hydroperoxide, had occurred. Decomposition of this hydroperoxide would also give rise to free radicals, which would in turn produce α -cumyl radicals, by attack on cumene, and eventually di- α -cumyl by subsequent dimerisation. The experiment was, therefore, repeated at 115° in duplicate, the reaction mixtures being kept under nitrogen in the dark, in order to minimise the formation of α -cumyl hydroperoxide. The results were qualitatively the same, except that no bisdiphenylmethyl ether was detected or isolated, traces of acetophenone were detected, and a trace of unidentified colourless solid (m. p. 152—166°) was isolated from the residue.

The results are shown in Table I.

Decomposition of Bisdiphenylmethyl Peroxide in Bromobenzene in the Presence of p-Benzoquinone.—*p*-Benzoquinone (m. p. 115°) was purified by steam distillation and crystallisation from light petroleum (b. p. 60—80°). The peroxide (6.089 g.) and benzoquinone (5.397 g.; 1½ equiv.) in bromobenzene (200 ml.) were boiled under reflux in a darkened flask for 137 hr. The black mixture was cooled (-30° for 4 hr.) and the black precipitate was collected, washed with light petroleum (b. p. 40—60°), and dried (3.4 g., m. p. 152—159°). A portion (0.426 g.) was sublimed at 135°/20 mm. for 30 hr. and the product (0.262 g.) was recrystallised from

ethanol to give quinhydrone (m. p. and mixed m. p. 170—171°). The original black material therefore contained quinhydrone (61%). Hence the recovery, based on 100% yield of hydrogen atoms from the peroxide, was 58%.

The bromobenzene solution was concentrated by distillation and the residue distilled to give two fractions: (i) b. p. 88—95°/0.1 mm.; 4.239 g., (ii) a pale yellow solid, b. p. 142—150°/0.1 mm., 0.389 g., and a residue, 1.360 g. Fraction (i) was a stable red liquid which, when seeded with benzophenone, solidified, the resultant solid rapidly darkening. The solid, in spite of the colour, had m. p. 44°, undepressed on admixture with benzophenone, and its spectrum was identical with that of pure benzophenone. It has been recorded that the colours of certain indicators dissolved in benzophenone appear only on solidification,¹¹ and the above remarkable colour change might be a phenomenon of this type. Fraction (ii) could not be identified.

Decomposition of Bisdiphenylmethyl Peroxide in Ethanolic Sodium Ethoxide.—Sodium (1.00 g.) in ethanol (50 ml.) was boiled under reflux to expel hydrogen. The peroxide (1.019 g.) was then added and the mixture boiled for 15 hr. The brown solution was concentrated and the residue was treated with ether (30 ml.) and water (50 ml.). After separation, the aqueous layer was extracted with ether. The combined ether extracts, on evaporation, left a brown solid (1.051 g.), a portion (0.441 g.) of which was chromatographed. Elution with light petroleum and light petroleum (b. p. 60—80°)—benzene (1 : 1) gave an unidentified yellow oil (0.022 g.). Elution with benzene gave benzophenone (0.057 g., m. p. and mixed m. p. 44°, identical infrared spectra), and ethanol gave diphenylmethanol (0.340 g., m. p. and mixed m. p. 62°).

Reaction of Benzophenone with Ethanolic Sodium Ethoxide.—Benzophenone (0.501 g.) was added to a boiling solution of sodium (1.00 g.) in ethanol (50 ml.), and the mixture was boiled for 15 hr. The mixture was worked up as described in the previous experiment to give diphenylmethanol (77%) and benzophenone (21%). A correction to the yield of benzophenone obtained from the decomposition of bisdiphenylmethyl peroxide in ethanolic sodium ethoxide could thus be made.

Decomposition of Bisdiphenylmethyl Peroxide in Pyridine.—A solution of the peroxide in pyridine was boiled under reflux (see Table 2) and the excess of solvent distilled off through a 10 in. helix-packed column. The residue was dissolved in benzene and basic material was extracted with hydrochloric acid. Concentration of the benzene solution gave a residue, which was chromatographed. Elution with light petroleum, benzene, and ethanol gave fractions which were identified by mixed m. p. and infrared spectrum. The main products were benzophenone and diphenylmethanol, although bisdiphenylmethyl ether was isolated in some cases. The pyridine and peroxide were rigorously purified in each case, but inconsistent results were obtained with this solvent. A complementary experiment, in which a pyridine solution of diphenylmethanol was boiled under reflux, indicated that benzophenone and the ether were formed, but in yields too low to account for the discrepancies. Pyridine 1-oxide was not isolated or detected.

Decomposition of Bisdiphenylmethyl Peroxide in 2 : 6-Lutidine.—A solution of the peroxide (2.987 g.) in 2 : 6-lutidine (100 ml.) was held at 115° for 8 days. Working up by the standard procedure gave benzophenone (1.22 moles/mole of peroxide) and diphenylmethanol (0.73 mole/mole of peroxide), *i.e.*, 98% recovery. No products of attack of the side-chains by free radicals were detected.

Chromatography of Bisdiphenylmethyl Peroxide.—The peroxide (0.018 mole) was adsorbed on alumina and eluted with benzene to give benzophenone (0.017 mole; m. p. and mixed m. p. 46°). Elution with chloroform gave diphenylmethanol (0.017 mole; m. p. and mixed m. p. 61—64°).

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¹¹ Terenin and Karyakin, *Doklady Akad. Nauk S.S.S.R.*, 1949, **68**, 345.