

445. The Reactions of Organic Peroxides. Part I. 2-Phenyl-2-butyl Hydroperoxide.

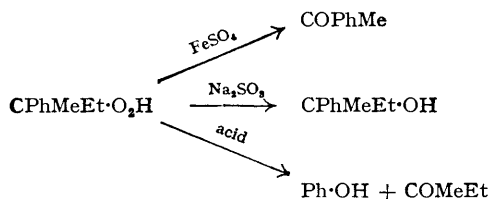
By E. G. E. HAWKINS.

2-Phenyl-2-butyl hydroperoxide has been prepared in good yield by the emulsion oxidation of *sec.*-butylbenzene. Reaction of the hydroperoxide with ferrous sulphate yields acetophenone, with sodium sulphite it gives phenylmethylethylcarbinol, whilst mineral acid causes formation of methyl ethyl ketone and phenol.

THE preparation of 2-phenyl-2-butyl hydroperoxide by oxidation of *sec.*-butylbenzene in the homogeneous liquid phase in ultra-violet light has recently been reported by Ivanov *et al.* (*Doklady Akad. Nauk. S.S.S.R.*, 1948, **59**, 905); the crude oxidate appeared to contain 5–6% of hydroperoxide.

Following the method used for the oxidation of *isopropyl*benzene and *sec.*-butyltoluene (the method developed by Armstrong, Hall, and Quin, *Nature*, 1949, in the press; The Distillers Company Ltd., B.P. 610,293), *sec.*-butylbenzene has now been oxidised in emulsion to yield a crude product containing *ca.* 30% of hydroperoxide. The oxidate was extracted with concentrated aqueous alkali, but only part of the hydroperoxide could be removed by this means. From the alkaline solution the hydroperoxide was obtained by treatment with carbon dioxide followed by benzene extraction.

The purified, distilled hydroperoxide had physical properties very similar to those given by the Russian authors, and its reaction with ferrous sulphate gave rise mainly to acetophenone as described by them.



Sodium sulphite reduced the hydroperoxide to phenylmethylethylcarbinol, whilst treatment with mineral acid brought about fission of a carbon-carbon linkage to give phenol and methyl ethyl ketone. This reaction is similar to that described for 2-phenyl-2-propyl hydroperoxide by Hock and Lang (*Ber.*, 1944, **77**, B, 257) in which phenol and acetone were formed.

EXPERIMENTAL.

(All m. p.s are uncorrected. Analyses are by Drs. Weiler and Strauss.)

sec.-Butylbenzene.—This was prepared by alkylation of benzene with but-1-ene (obtained by dehydration of *n*-butanol with alumina at 400°; cf. Pines, *J. Amer. Chem. Soc.*, 1933, **55**, 3892) in the presence of sulphuric acid as catalyst (Corson and Pines, *ibid.*, 1936, **58**, 919). The mixture was kept at about 10° and only $\frac{2}{3}$ rd of the stoichiometric quantity of butene was used, so as to keep di-substitution at a minimum. The fraction finally taken had b. p. 172–175°/764 mm., n_D^{20} 1.4898.

Oxidation of sec.-Butylbenzene.—(i) The hydrocarbon (130 g., 150 c.c.), water (300 c.c.), sodium carbonate (3 g.), and stearic acid (0.25 g.) were stirred at 85°, and a slow stream of oxygen passed through the solution. Reaction was slow and at an average rate of absorption of 350 c.c. of oxygen per hour the concentration of hydroperoxide reached 30% (on the oil phase) in about 120 hours. The peroxide content, as determined by potassium iodide-acetic acid reagent, began to fall again after this time.

The organic layer was separated from the aqueous phase, and extracted three times with strong aqueous sodium hydroxide. The hydroperoxide was obtained from the combined alkaline extracts by passage of carbon dioxide and extraction with benzene, followed by evaporation of the benzene under reduced pressure in an atmosphere of nitrogen. Distillation of the residue yielded an initial small fraction of acetophenone, identified as its 2:4-dinitrophenylhydrazone, followed by the main fraction (5 g.), b. p. 60°/1.5 × 10⁻² mm. This fraction contained 61.5% of hydroperoxide (determined iodometrically).

The material remaining after alkali extraction of the organic layer still contained much peroxide and was distilled directly to give unreacted hydrocarbon (51.1 g.) as well as the following fractions: (a) (12.9 g.), b. p. 56–58°/3 × 10⁻² mm. (containing acetophenone and 30% of hydroperoxide); (b) (9.0 g.), b. p. 58–66°/3 × 10⁻² mm. (containing 66% of hydroperoxide); and (c) (13.5 g.), b. p. 66–68°/3 × 10⁻² mm. (containing 89% of hydroperoxide).

(ii) *sec.*-Butylbenzene was hydrogenated over Raney nickel at atmospheric pressure to saturate traces of material having olefinic side-chains. Using quantities and conditions of oxidation as before a concentration of 25% of hydroperoxide (on the organic phase) was reached in only 47 hours. The organic layer was separated and distilled directly, giving fractions similar to those described in (i).

2-Phenyl-2-butyl Hydroperoxide.—A portion of the peroxide concentrate was dissolved in light

petroleum (b. p. 40—60°) and treated with 45% sodium hydroxide solution. The solid sodium salt of the hydroperoxide was filtered off and washed with petroleum, and from it the free hydroperoxide was regenerated by treatment of an aqueous suspension with carbon dioxide. Distillation gave material, b. p. 58—58.5°/0.01 mm., n_D^{20} 1.5206 (Found: C, 72.6, 72.7; H, 8.71, 8.83%; peroxide equivalent, 162. Calculated for $C_{10}H_{14}O_2$: C, 72.3; H, 8.43%; peroxide equivalent, 166).

Reaction with ferrous sulphate. The hydroperoxide (5 g.) was stirred with ferrous sulphate solution (10 g. of crystalline salt in 20 c.c. of water) for one hour at water-bath temperature. The solution, which contained a brown precipitate of a ferric compound, was extracted with ether, the ethereal extract was evaporated, and the residue (3.9 g.) distilled. Acetophenone, b. p. 200—204°, was the only product (the 2:4-dinitrophenylhydrazone had m. p. 244—245°, unaltered by admixture with an authentic specimen).

Reaction with sodium sulphite. The hydroperoxide (5 g.) and sodium sulphite (10 g. in 20 c.c. of water) were stirred for 3—4 hours on the water-bath. On extraction of the product with ether, followed by removal of the solvent and distillation, only phenylmethylethylcarbinol, b. p. 53—54°/0.1 mm. (4.0 g.), was obtained.

This yielded a *phenylurethane*, m. p. 89—90° (Found: C, 75.9; H, 7.29; N, 4.99. $C_{17}H_{19}O_2N$ requires C, 75.8; H, 7.06; N, 5.20%), and an *α -naphthylurethane*, m. p. 129—130.5° (Found: C, 78.4; H, 6.27; N, 4.71. $C_{21}H_{21}O_2N$ requires C, 78.99; H, 6.58; N, 4.39%).

Reaction with mineral acid. The hydroperoxide (10 g.) and sulphuric acid (10%; 50 c.c.) were stirred for 4 hours on the water-bath. After removal of the solvent from the ethereal extract of the solution, distillation gave: fraction 1 (1.0 g.), b. p. 70—80°; fraction 2 (0.6 g.), b. p. 80—165°; fraction 3 (5.8 g.), b. p. 165—185°; and residue (0.3 g.).

Fraction 1 was methyl ethyl ketone (2:4-dinitrophenylhydrazone, m. p. 115—116° unchanged on admixture with a synthetic sample). Fraction 2 contained both methyl ethyl ketone and phenol. Fraction 3 consisted of phenol (benzoate, m. p. and mixed m. p. 69—70°).

The author thanks his colleagues for discussions and in particular Dr. D. C. Quin and Dr. R. H. Hall for details of the method of emulsion oxidation.

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[Received, April 8th, 1949.]