The higher-boiling alcohols, being soluble in ether, are apt to be carried through the ether extraction. The presence of these alcohols in the residue inhibits good crystal formation of the ester. This difficulty may be overcome by mixing and melting equimolar concentrations of the acid chloride with the higher-boiling alcohols.

Table I is a composite of analytical data with the procedure just described for the preparation of the esters of the maleic acid anhydride addition product of *l*-pimaric acid.

Acknowledgment.—The author wishes to thank Ray V. Lawrence of this Division for his suggestions and interest throughout this work and S. M. Stark, Jr., of the Analytical, Physical Chemical and Physical Division of the Southern Regional Research Laboratory, for making the combustion analyses.

Summary

The preparation of the monoacid chloride of the maleic acid anhydride addition product of *l*-pimaric acid is described. The methyl-, ethyl-, *n*-propyl- and *n*-butyl esters of the maleic acid anhydride addition product of *l*-pimaric acid have been prepared by several methods. The synthesis of these esters by the method involving the preparation of the monoacid chloride of the addition product proved less cumbersome than the other methods; it obviated the necessity of using esters of abietic acid, and the yields were practically quantitative.

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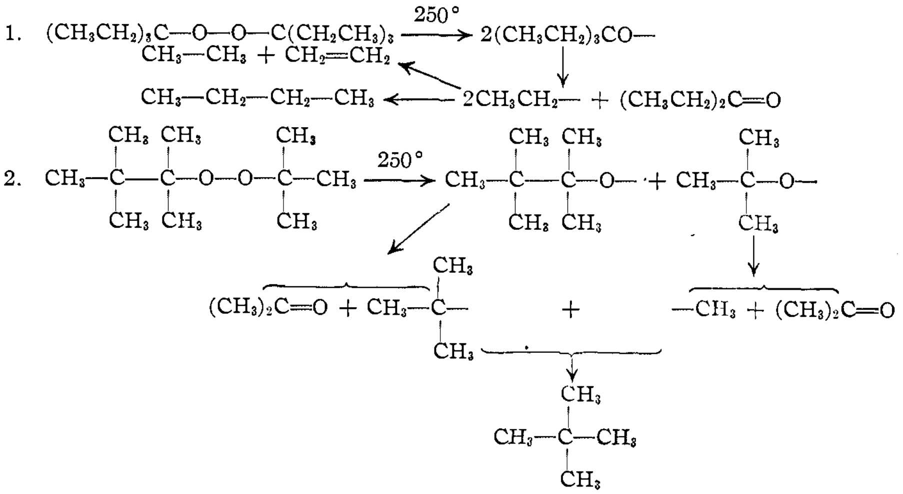
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Synthesis and Thermal Decomposition of Di-triethylmethyl, *t*-Butyl Pentamethylethyl and *t*-Butyl 1-Methylcyclohexyl-1 Peroxides[1]

BY NICHOLAS A. MILAS AND LLOYD H. PERRY[1a]

In the previous papers[2] mention was made of the fact that comparatively few tertiary alkyl peroxides and hydroperoxides are known. In order to establish the generality of the original reaction[3] and the mode of the thermal decomposition of ditertiary alkyl peroxides, a number of higher tertiary alkyl peroxides and hydroperoxides have been synthesized and are herein reported. The ditertiary alkyl peroxides were best prepared from the corresponding tertiary alkyl hydroperoxides and tertiary alkyl hydrogen sulfates. For example, di-triethylmethyl peroxide was prepared from triethylmethyl hydrogen sulfate and triethylmethyl hydroperoxide, *t*-butyl pentamethylethyl peroxide from pentamethylethyl hydrogen sulfate and *t*-butyl hydroperoxide and *t*-butyl 1-methylcyclohexyl-1 peroxide from 1-methylcyclohexyl-1 hydrogen sulfate and *t*-butyl hydroperoxide.

When di-triethylmethyl peroxide was passed through a tube packed with glass wool and maintained at 250°, diethyl ketone and *n*-butane were the main products formed with some ethane and ethylene as by-products. Similarly, *t*-butyl pentamethylethyl peroxide gave, under the same conditions, acetone and neopentane as the chief pyrolysis products. These results may be best interpreted by the following sets of reactions



The pyrolysis of *t*-butyl 1-methylcyclohexyl-1 peroxide (0.134 mole) at 250° yielded acetone (0.117 mole, 87.4%), 3-methylheptanone-2 (0.066 mole, 49.2%), 3,4-di-*n*-butyl hexanedione-2,5 (0.020 mole, 30%) and ethane (0.033 mole, 24.6%) as the only products. These products may be accounted for by assuming a rearrangement of the 1-methylcyclohexyl-1-oxy radical (II) in such a manner that a hydrogen atom migrates from one of the carbon atoms in the cyclohexane ring beta to the oxygen atom simultaneously with the opening of the ring at the other beta carbon atom to form the radical (IV) which may either combine with the methyl radical resulting from the decomposition of the *t*-butoxy radical (III), to form 3-methyl heptanone-2 (V), or dimerize to form 3,4-

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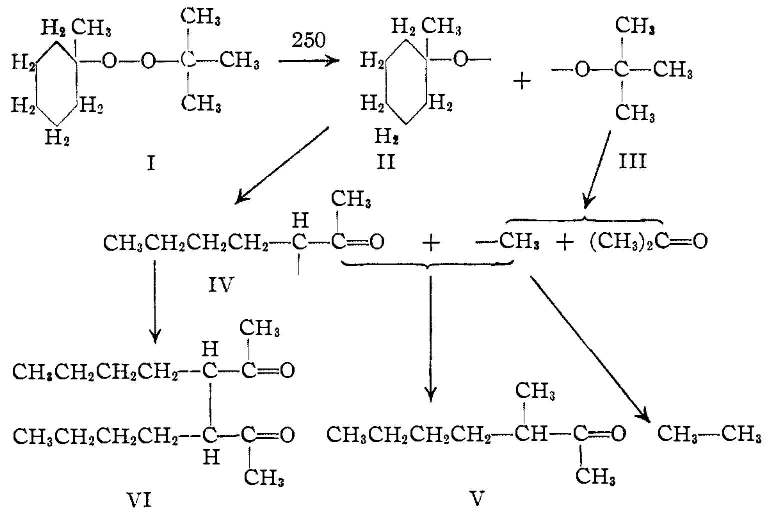
(1) Studies in Organic Peroxides. XI.

(1a) Present address: Union Bay State Chemical Company.

(2) Milas and Surgenor, THIS JOURNAL, **68**, 205, 643 (1946).

(3) Milas, U. S. Patent 2,223,807, Dec. 3, 1940.



di-*n*-butyl hexanedione-2,5 (VI). The presence of ethane in the pyrolysis products is also accounted for by the dimerization of the free radical (IV) leaving excess methyl radicals to dimerize.

Experimental

Triethylmethyl Hydroperoxide.—This hydroperoxide was prepared[4] from 70% sulfuric acid, triethylcarbinol (b. p. 141–142°)[5] and 27% hydrogen peroxide. It was further purified by fractionation through a three-inch Vigreaux column and the fraction boiling at 27.5–28° (2 mm.) was collected and analyzed; m. p. 2–3°; n^{20}_D 1.4379; d^{20}_4 0.914.

Anal. Calcd. for $C_7H_{16}O_2$: C, 63.6; H, 12.1; (O), 12.12. Found: C, 63.2; H, 12.2; O, 12.06.

Di-triethylmethyl Peroxide.—Triethylmethyl hydrogen sulfate was prepared by adding dropwise with stirring 52 g. (0.37 mole) of 70% sulfuric acid to 43 g. (0.37 mole) of triethylcarbinol maintained at 0 to −5°. To this mixture was added, keeping the temperature and stirring the same, 49 g. (0.37 mole) of 95% triethylmethylhydroperoxide. The reaction mixture was allowed to stir for twenty-four hours at −3°, then the non-aqueous peroxide layer separated out, washed with water and dried. After removing the low boiling fraction under reduced pressure (100 mm.) from the crude peroxide (51 g.), the residue (20 g.) was distilled in a modified Hickman still at a bath temperature of 38–40° (20 μ) and a fraction (15 g.) was collected and analyzed; n^{20}_D 1.4405; d^{20}_4 0.882.

Anal. Calcd. for $C_{14}H_{30}O$: C, 73.1; H, 13.0. Found: C, 73.2; H, 12.7.

The low boiling fraction was identified as a mixture of 3-ethylpentene-2 [b. p. 92–96°; d^{20}_4 0.736; dibromide, b. p. 82–84° (3.5 mm.), n^{20}_D 1.4998; d^{20}_4 1.538][6] and diethyl ketone (2,4-dinitrophenylhydrazone, m. p. 155.5–156.1°).[7]

When a sample (12 g.) of di-triethylmethyl peroxide was reduced catalytically in ethanol using Raney nickel at 120° and at a hydrogen pressure of 1190 lb., a mixture of products was obtained which yielded 3.5 g. of 3-ethylpentane and 4 g. of triethylcarbinol.

Pyrolysis of Di-triethylmethyl Peroxide.—Di-triethylmethyl peroxide (15 g., 0.065 mole) was pyrolyzed at 250° using the apparatus described in a previous paper.[2] The pyrolysis products were as follows: (1) a liquid (12 g.) collected in an ice trap gave on fractionation 7 g. (0.081 mole, 61% yield) of diethyl ketone, b. p. 100–101.5°, semicarbazone, m. p. 138–139° and 4 g. of unidentified viscous residue; (2) a liquid condensate (2 g., 0.035 mole) of *n*-butane, b. p. −2 to 0°.

Anal. Calcd. for C_4H_{10}: O_2/C_4H_{10}, 6.5; CO_2/C_4H_{10}, 4.0. Found: O_2/gas, 7.1; CO_2/gas, 4.2.

(3) A gas (1.2 liters) which had an analysis corresponding to 29% ethane and 5% ethylene.

Pentamethylethylhydroperoxide.—Pentamethylethylhydrogen sulfate was prepared by adding dropwise with stirring at 0 to −5° 65 g. (0.46 mole) of 70% sulfuric acid to 60 g. (0.45 mole) of pentamethylethanol monohydrate m. p. 82–83°.[8,9] To the above mixture was then added with stirring 59 g. (0.46 mole) of 27% hydrogen peroxide. During the reaction, it was necessary to cool the reaction mixture intermittently to prevent the temperature from rising above 30°. Stirring was continued overnight at room temperature, then the peroxide non-aqueous layer separated, washed with water and dried; yield of the crude product, 40 g. having an active oxygen of 8.31% corresponding to a yield of 69%. Attempts to purify this hydroperoxide by fractionation under reduced pressure or through the formation of the barium salt were unsuccessful. A solid barium derivative was obtained with a purity of slightly over 50%.

***t*-Butyl Pentamethylethyl Peroxide.**—To pentamethylethyl hydrogen sulfate, maintained at 0 to −5° and prepared by adding 46 g. (0.33 mole) of 70% sulfuric acid to 40 g. (0.30 mole) of pentamethylethanol monohydrate, was added with stirring in the course of one hour 30 g. (0.33 mole) of *t*-butyl hydroperoxide. Stirring was continued at room temperature until the top layer gave a negative active oxygen test with potassium iodide in glacial acetic acid. The top layer was then removed, washed three times with small portions of water containing suspensions of magnesium carbonate and dried over anhydrous magnesium sulfate; yield of the crude product, 45 g. This was fractionated under reduced pressure through a two-foot Podbielniak column and the fraction (23 g.) boiling at 27–27.5° (4 mm.) collected and analyzed; n^{20}_D 1.4150; d^{20}_4 0.827.

Anal. Calcd. for $C_{11}H_{24}O_2$: C, 70.1; H, 12.9. Found: C, 70.5; H, 12.9.

Pyrolysis of *t*-Butyl Pentamethylethyl Peroxide.—*t*-Butyl pentamethylethyl peroxide (20 g., 0.106 mole) was pyrolyzed at 250° at an average rate of about 0.095 g. per minute. The pyrolysis products yielded 10 g. (0.19 mole) of acetone (b. p. 56–56.5°; n^{24}_D 1.3580; d^{20}_4 0.790) and 4 g. (0.06 mole) of neopentane, b. p. 8–10°. *Anal.* Calcd. for C_5H_{12}: O_2/C_5H_{12}, 8.0; CO_2/C_5H_{12}, 5.0. Found: O_2/gas, 8.4; CO_2/gas, 5.0. A small amount of a gaseous mixture was also obtained. This consisted of about 65% ethane and 35% of neopentane.

1-Methylcyclohexyl-1 Hydroperoxide.—1-Methylcyclohexyl-1 hydrogen sulfate was prepared by adding dropwise with stirring 51 g. (0.36 mole) of 70% sulfuric acid to 38 g. (0.33 mole) of 1-methylcyclohexanol-1 [b. p. 69–70° (30 mm.); m. p. 24–25°] maintained at 0 to −5°. To this mixture was added, keeping the temperature and stirring the same, 46 g. (0.36 mole) of 27% hydrogen peroxide. Stirring was continued for six hours longer at 25–30° then the mixture was extracted with olefin-free petroleum ether, dried and the petroleum ether removed. A product (34 g.) was obtained containing 70% hydroperoxide. Further purification was not possible without appreciable decomposition. The diperphthalate was made following

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[4] Milas and Surgenor, THIS JOURNAL, **68**, 205 (1946).

[5] Weigert, *Ber.*, **36**, 1009 (1903).

[6] *Cf.* Soday and Boord, THIS JOURNAL, **55**, 3300 (1933).

[7] Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1941, p. 376.

[8] Adams and Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1941, Coll. Vol. I, p. 459.

[9] Henry, *Compt. rend.*, **143**, 20 (1906).

TABLE I

LIQUID PYROLYSIS PRODUCTS OF *t*-BUTYL 1-METHYLCYCLOHEXYL-1 PEROXIDE

Fraction	Amt., g.	B. p. or m. p., °C.	$n^{20}D$	d^{20}_4	Product
I	6.8	56 - 58	1.3588	0.790	Acetone
II	9.0	48 - 52 (15 mm.) 154 -156 (760 mm.)	1.4190	.825	3-Methylheptanone-2
III	4.0	93 - 95 (2.5 mm.) 55.8- 56.8	1.4430	.900	3,4-Di-*n*-butyl hexanedione-2,5

the procedure described elsewhere.[10] This diperester was recrystallized from ethyl ether; m. p. 81–82°.

Anal. Calcd. for $C_{22}H_{30}O_6$: C, 67.7; H, 7.51; (O), 8.20. Found: C, 67.5; H, 7.51; O, 8.07.

***t*-Butyl 1-Methylcyclohexyl-1 Peroxide.**—To 1-methylcyclohexyl-1 hydrogen sulfate, prepared from 50 g. (0.33 mole) of 63% sulfuric acid and 34 g. (0.30 mole) of 1-methylcyclohexanol-1, was added dropwise with stirring at 0 to −5° 30 g. (0.33 mole) of *t*-butyl hydroperoxide. Stirring was continued for eight hours longer at 15–20°. The top non-aqueous peroxide layer was then removed, washed with water and dried; yield 41 g. This was fractionated under reduced pressure through a three-inch Vigreaux column and the fraction (21 g., 38% yield) boiling at 28–29° (2.5 mm.) collected and analyzed; $n^{20}D$ 1.4350; d^{20}_4 0.881.

Anal. Calcd. for $C_{11}H_{22}O_2$: C, 70.8; H, 11.9. Found: C, 70.5; H, 12.1.

Pyrolysis of *t*-Butyl 1-Methylcyclohexyl-1 Peroxide.—This peroxide (25 g., 0.134 mole) was pyrolyzed at 250° at an average rate of about 0.119 g. per minute. A gas (594 cc.) was obtained which proved to be ethane.

Anal. Calcd. for C_2H_6: O_2/C_2H_6, 3.5; CO_2/C_2H_6, 2.0. Found: O_2/gas, 3.6; CO_2/gas, 1.9.

The only other product obtained was a liquid (22.5 g.) which was fractionated and the results tabulated in Table I.

Identification of Fraction II.—Fraction II was identified as follows: (1) Fraction II gave a positive iodoform test and a sodium bisulfite addition product; semicarbazone, m. p. 80–81°.

Anal. Calcd. for $C_9H_{19}ON_3$: N, 22.7. Found: N, 23.0.

(2) Oxidation of fraction II (5 g.) by the method of Sandburn and Bousquet[11] gave an acid (4 g., 79% yield) which boiled at 71–72.5° (3.5 mm.); $n^{20}D$ 1.4208; d^{20}_4 0.918; neut. eq., 127: calcd. for $C_7H_{14}O_2$, 130: anilide, m. p. 94–95.5° (98°).[12]

(3) 4-Methylheptanone-2 was synthesized[13] and its properties compared with those of fraction II; b. p. 154–156°; $n^{20}D$ 1.4152; d^{20}_4 0.822; semicarbazone, m. p. 104–105°. Since the melting point of the semicarbazone of 4-methylheptanone-2 is higher than that of the semicarbazone of fraction II, the 3-methylheptanone-2 was synthesized by the method of Powell.[14] This ketone was found to have a b. p. of 159–159.5° and a d^{20}_4 0.819. It formed a semicarbazone, m. p. 82.5–83.5°; mixed m. p. with the semicarbazone of fraction II, 80.5–82°. Therefore, our evidence seems to indicate that the ketone of fraction II is 3-methylheptanone-2. All other methylheptanones and octanone-2 have been considered and eliminated.

Identification of Fraction III.—This fraction was crystallized by cooling and the solid recrystallized first from 95% ethanol, then from petroleum ether; m. p. 55.8–56.8°.

Anal. Calcd. for $C_{14}H_{26}O_2$: C, 74.3; H, 11.6. Found: C, 74.4; H, 11.8.

Dioxime, m. p., 212.5–213.5°.

Anal. Calcd. for $C_{14}H_{28}O_2N_2$: N, 10.9. Found: N, 10.9.

The diketone gave positive iodoform and pyrrole tests. An attempt to separate the pyrrole chromatographically or by other means produced a green substance which was difficult to purify.

Oxidation of the Diketone.—About 0.3 g. of the diketone was oxidized by the method of Rupe and Kuenzy.[11,15] A yield of 0.25 g. (83%) of the dicarboxylic acid was obtained; m. p. 169–171°; neut. eq., 114: calcd. for the symmetrical di-*n*-butylsuccinic acid, 115. Our evidence, so far, seems to indicate that the diketone obtained in fraction III may be 3,4-di-*n*-butylhexanedione-2,5.

Acknowledgment.—The authors wish to thank the Union Bay State Chemical Company for financial support in carrying out this investigation.

Summary

1. Triethylmethyl, pentamethylethyl and 1-methylcyclohexyl-1 hydroperoxides have been synthesized.

2. Di-triethylmethyl, *t*-butyl pentamethylethyl and *t*-butyl 1-methylcyclohexyl-1 peroxides have also been synthesized.

3. The thermal decomposition of di-triethyl methyl, *t*-butyl pentamethylethyl and *t*-butyl 1-methylcyclohexyl-1 peroxides at 250° has been studied and the products of decomposition isolated and identified.

4. A tentative explanation of the mode of decomposition is given.

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(10) Milas and Surgenor, THIS JOURNAL, **68**, 642 (1946).

(11) Sandburn and Bousquet, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1941, Coll. Vol. I, p. 526.

(12) Reichstein and Trivelli, *Helv. Chim. Acta*, **15**, 258 (1932).

(13) Clarke, *Am. Chem. J.*, **39**, 90 (1908).

(14) Powell, THIS JOURNAL, **46**, 2517 (1924).

(15) Rupe and Kuenzy, *Helv. Chim. Acta*, **14**, 701 (1931).