followed by three washings of 200 cc. of water and dried over anhydrous magnesium sulfate. Finally, the mixture was filtered and the filtrate subjected to a high vacuum at 50–60° in order to remove the volatile products. Yield of the crude product was 450 g. (99%); $d^{20}_4$ 1.026. A portion of this perester was distilled under reduced pressure and the product, a pale yellow liquid, boiling at 75–77° (2 mm.) collected and analyzed. The physical constants and analytical data for this and seven other peresters synthesized essentially by the same procedure are summarized in Table I.

**Reaction of *t*-Butyl Perbenzoate with Sodium Methylate.**—To 100 cc. of absolute methanol containing 5.2 g. of sodium and maintained at 5°, was added in the course of five minutes 40 g. of *t*-butyl perbenzoate in 200 cc. of chloroform. After ten minutes of standing, the mixture was shaken with 500 cc. of water, and the organic layer separated and washed with 100 cc. of water and dried over magnesium sulfate. The combined washings were neutralized with sulfuric acid, extracted with ether several times, the ether extracts dried and the ether removed. The residue (12.6 g.) contained 71% *t*-butyl hydroperoxide corresponding to a yield of 8.9 g. The chloroform layer was fractionated and the fraction boiling at 39–43° (1 mm.) was collected. A yield of 23.2 (83%) of methyl benzoate was obtained having the following constants: $d^{20}_4$ 1.087; $n^{20}D$ 1.5148. These values agree well with those given in the literature.

**Acknowledgment.**—The authors wish to thank Mr. C. O. Ewing for assistance in some of the experiments and the Union Bay State Chemical Company for financial aid in carrying out this investigation.

## Summary

1. Eight *t*-butyl peresters have been synthesized and fully characterized.

2. The reaction of sodium methylate and *t*-butyl perbenzoate was studied and found to yield *t*-butyl hydroperoxide and methyl benzoate.

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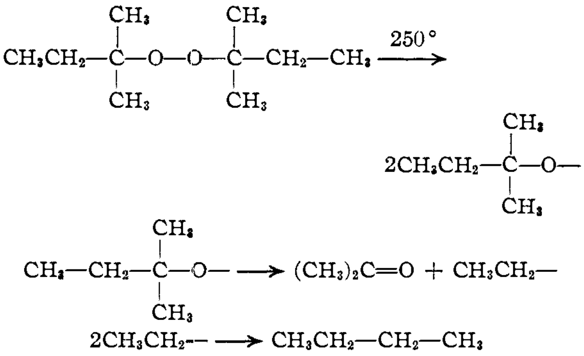
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# Studies in Organic Peroxides. X. *t*-Amyl Hydroperoxide and Di-*t*-amyl Peroxide

BY NICHOLAS A. MILAS AND DOUGLAS M. SURGENOR[1]

In a recent paper,[2] we have discussed the synthesis and chemistry of organic peroxides containing the *t*-butyl group. The present paper extends our investigations to include peroxides containing the *t*-amyl group. *t*-Amyl hydroperoxide can be prepared at low temperatures by the interaction of *t*-amyl hydrogen sulfate and concentrated hydrogen peroxide.

Di-*t*-amyl peroxide can be prepared either from *t*-amyl hydrogen sulfate and *t*-amyl hydroperoxide or directly from *t*-amyl hydrogen sulfate and hydrogen peroxide by increasing the concentration of sulfuric acid. The chemical behavior of this peroxide parallels that of di-*t*-butyl peroxide. When pyrolyzed at 250°, di-*t*-amyl peroxide gives mainly acetone and *n*-butane with small amounts of methyl ethyl ketone and a gas, consisting of about 80% ethane and 20% propane. The main pyrolysis products of this peroxide may be best explained by the assumption of the intermediate formation of free radicals.



$$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_3 \xrightarrow{250^\circ} 2CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-O-$$

$$CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-O- \longrightarrow (CH_3)_2C=O + CH_3CH_2-$$

$$2CH_3CH_2- \longrightarrow CH_3CH_2-CH_2-CH_3$$

These results seem to indicate that of the three groups attached to the tertiary carbon atom in di-tertiary amyl peroxide, the heavier group splits off preferentially as a free radical which dimerizes to form butane. Additional evidence to support this finding has been produced in the synthesis and pyrolysis of *t*-butyl pentamethylethyl peroxide and other higher di-tertiary alkyl peroxides.[3]

## Experimental

***t*-Amyl Hydroperoxide.**—*t*-Amyl hydrogen sulfate was prepared at 0° with stirring by adding in the course of one hour 880 g. (10 moles) of *t*-amyl alcohol to 1400 g. (10 moles) of 70% sulfuric acid. To this mixture was then added at 0° with stirring 1230 g. (10 moles) of 27% hydrogen peroxide over a period of two and three-quarters hours. The resulting mixture was allowed to stand at 5° for twenty-four hours, then the organic layer separated and neutralized with a suspension of magnesium carbonate, followed by washing with water and drying; yield of the crude product (55.6% pure), 715 g. To further purify this hydroperoxide, the crude product was extracted at 5° with 30% potassium hydroperoxide and the non-acidic portion removed by extraction with olefin-free petroleum ether. The alkali extract was then acidified at 10° with 70% sulfuric acid, and the hydroperoxide recovered and fractionated under reduced pressure and the fraction boiling at 26° (3.5 mm.) collected and analyzed; $d^{20}_4$ 0.903; $n^{20}D$ 1.4161.

*Anal.* Calcd. for $C_5H_{12}O_2$: C, 57.65; H, 11.61; (O), 15.35. Found: C, 57.6, 57.6; H, 11.4, 11.6; (O), 15.33, 15.35, 15.52.

***t*-Amyl Perbenzoate.**—This perester was synthesized by a procedure similar to that used by Milas and Surgenor.[4] A yield of 66% of the crude perester was obtained having

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[1] Present address: Harvard Medical School, Boston, Mass.

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

[3] Milas and Perry, unpublished results.

[4] Milas and Surgenor, THIS JOURNAL, **68**, 642 (1946).

a $d^{20}_4$ of 1.030. A sample of this was distilled in a molecular still at bath temperature of 55° (13 $\mu$) and the distillate analyzed; $d^{20}_4$ 1.037; $n^{20}_D$ 1.5010.

*Anal.* Calcd. for $C_{13}H_{16}O_3$: C, 69.20; H, 7.74; (O), 7.68. Found: C, 69.1, 69.0; H, 7.79, 7.54; (O), 7.44, 7.51.

**Di-*t*-amyl Peroxide.**—*t*-Amyl hydrogen sulfate was prepared by adding at 5° with stirring 176 g. (2 moles) of *t*-amyl alcohol to 140 g. (1 mole) of 70% sulfuric acid. To this mixture was then added simultaneously in the course of four hours with vigorous stirring, keeping the temperature at 5°, 126 g. (1 mole) of 27% hydrogen peroxide and 341 g. of concentrated sulfuric. The reaction mixture separated into two layers; the organic layer was removed, washed with water, dried, and distilled through a Vigreux column under reduced pressure and the fraction (43 g.) boiling at 44° (10 mm.) collected and analyzed; $d^{20}_4$ 0.821; $n^{20}_D$ 1.4095.

*Anal.* Calcd. for $C_{10}H_{22}O_2$: C, 68.91; H, 12.72. Found: C, 68.8, 69.1; H, 12.4, 12.5.

**Pyrolysis of Di-*t*-amyl Peroxide.**—Di-*t*-amyl peroxide (20 g.) was pyrolyzed at 250° using the apparatus described in a previous paper.[2] The pyrolysis products were as follows: (1) A liquid (12.4 g.) collected in an ice trap, 11.5 g. of which was acetone, b. p. 55–56°; 2,4-dinitrophenylhydrazone; m. p. 125.5–126.5°. From the residue (approx. 1 g.) was obtained a 2,4-dinitrophenylhydrazone, m. p. 115.5–117° which agrees with the melting point of the same derivative of methyl ethyl ketone. (2) A liquid condensate (4.1 g.) in the carbon dioxide ice trap having a b. p. of −1 to 0° and by analysis proved to be *n*-butane.

*Anal.* Calcd. for $C_4H_{10}$: $O_2/C_4H_{10}$, 6.5; $CO_2/C_4H_{10}$ 4.0. Found: $O_2$/gas, 6.9; $CO_2$/gas, 3.9.

(3) A gas (360 cc.) which had an analysis corresponding to about 80% ethane and 20% propane.

**Acknowledgment.**—The authors wish to thank Mr. C. O. Ewing for assistance in some of the experiments and the Union Bay State Chemical Company for financial aid in carrying out this investigation.

## Summary

1. *t*-Amyl hydroperoxide and di-*t*-amyl peroxide have been synthesized and some of their properties determined.

2. *t*-Amyl perbenzoate has been prepared from *t*-amyl hydroperoxide.

3. The thermal decomposition of di-*t*-amyl peroxide has been found to lead mainly to the formation of acetone and *n*-butane. These results are best accounted for by the formation of intermediate free radicals.

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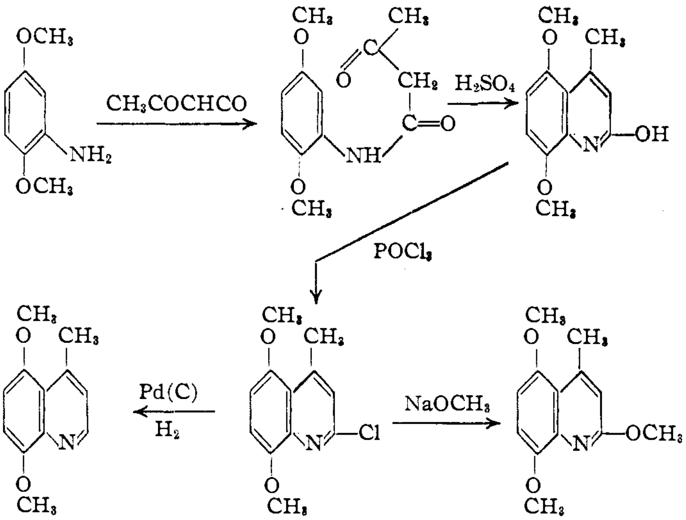
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF INDIANA UNIVERSITY]

# Substituted Lepidines[1]

BY C. E. KASLOW AND N. B. SOMMER[2,3]

A useful method for the synthesis of substituted lepidines has been developed. As an illustration of the reactions described in the present paper, the following equations may be cited which show the synthesis of 5,8-dimethoxy- and 2,5,8-trimethoxylepidine.

The first step in this synthesis involves the treatment of a primary aromatic amine with ketene dimer which formed the substituted acetoacetanilides in 78–98% yields. The yields by this method were much higher than those obtainable by the action of an aryl amine on ethyl acetoacetate which reaction sometimes leads to the formation of $\beta$-arylaminocrotonates.[4] The other steps in the syntheses are well-known reactions and proceed smoothly so that the substituted lepidines are obtained from the primary aromatic amines in over-all yields which range from 64–80%. These yields are an improvement over previous direct methods of synthesis.[5]



In the experimental part of this paper, there are described the preparation of six substituted lepidines and two benzoquinolines by use of the above synthetic scheme. The intermediate substituted acetoacetanilides, carbostyrils and 2-chlorolepidines were also isolated and characterized.

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(1) Presented in part before the Division of Organic Chemistry, American Chemical Society, New York, N. Y., September 13, 1944.

(2) Abstracted from a thesis submitted to the Faculty of the Graduate School in partial fulfillment of the requirements for the degree, Doctor of Philosophy, in the Department of Chemistry, Indiana University.

(3) Present address: American Cyanamid Company, Stamford, Connecticut.

(4) Krahler and Burger, THIS JOURNAL, **64**, 2417 (1942).

(5) Campbell and Schaffner, *ibid.*, **67**, 86 (1945).