

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

Studies in Organic Peroxides. IX. *t*-Butyl PerestersBY NICHOLAS A. MILAS AND DOUGLAS M. SURGENOR¹

Organic peresters cannot be classed as derivatives of organic peracids and alcohols, but rather as derivatives of organic acids and hydroperoxides. Heretofore, attempts to prepare peresters from peracids have been unsuccessful.² Furthermore, when peresters are saponified, the products formed are not peracids and alcohols, but acids and hydroperoxides.

Only six peresters are definitely known: ethyl peracetate,³ dimethyl,⁴ diethyl³ and diisopropyl⁵ perterephthalates, *s*-methyl perester-*t*-methyl camphorate⁶ and *trans*-9-decalyl perbenzoate.⁷ Of these, the first five have been prepared from the barium salt of the hydroperoxide and the corresponding acid chloride, while the last one was prepared in pyridine from the hydroperoxide and benzoyl chloride. No tertiary alkyl peresters are known and the present paper describes the synthesis and some of the properties of eight *t*-butyl peresters. These peresters have been prepared by adding simultaneously the acid chloride and aqueous alkali to cold *t*-butyl hydroperoxide.

properties as polymerization catalysts.⁸ Due to their exceptional stability, they liberate iodine slowly from an acidified solution of potassium iodide. Therefore, estimation of the active oxygen in these peresters was best accomplished in an acetone-glacial acetic acid-sodium iodide solution with ample time, three to four hours, allowed for the completion of the reaction. In glacial acetic acid alone, with adequate blanks, the values obtained were abnormally high, two to six per cent. higher than those predicted from the structure of the peresters. With the crystalline peresters, these high values were attributed at first to the *t*-butyl hydroperoxide of crystallization, but this explanation was discarded because catalytic hydrogenation and ultimate analyses gave normal results, and Zerewitinoff determinations showed no active hydrogen. Whether the increased oxidation of sodium iodide was due to an induced auto-oxidation which was inhibited by the presence of acetone, it is not definitely known at present.

TABLE I
PHYSICAL CONSTANTS AND OTHER DATA OF *t*-BUTYL PERESTERS

| Perester | Formula | Yield, % | B. p. or m. p., °C. | Press. (mm.) | <i>d</i> ₄ ²⁰ | <i>n</i> _D ²⁰ | Analyses, % | | | | | | | |
|------------------------------|--|-------------|---------------------------|-----------------|-------------------------------------|-------------------------------------|-------------|-------|--------|-------|--------|-------|-------------------------|-------------------|
| | | | | | | | C | | H | | Act. O | | H ₂ (Pd, Pt) | |
| | | | | | | | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| Perbenzoate | C ₁₁ H ₁₄ O ₃ | 99 | 75-77 | 2 | 1.043 | 1.5007 | 68.03 | 68.2 | 7.26 | 7.39 | 8.24 | 8.25 | 1.0 | 1.03 ^a |
| | | | | | | | | 67.9 | | 7.53 | | 8.29 | | 4.1 ^b |
| Perfuroate | C ₉ H ₁₂ O ₄ | 61 | 40-49° | 2.5μ | 1.092 | 1.4747 | 58.68 | 58.6 | 6.57 | 6.62 | 8.68 | 7.68 | ... | ... |
| | | | | | | | | 58.9 | | 6.77 | | 7.61 | | |
| | | | | | | | | | | | | 7.61 | | |
| Perstearate ^d | C ₂₂ H ₃₄ O ₃ | 52 | 86° 14-16.5 | 0.3μ | ... | ... | 74.10 | 74.10 | 12.43 | 12.4 | 4.49 | 3.92 | 1.0 | 1.02 ^b |
| | | | | | | | | 73.80 | | 12.2 | | 3.94 | | |
| Perundecylenate ^e | C ₁₅ H ₂₈ O ₃ | 81 | 76° | 0.07 | 0.901 | 1.4453 | 70.27 | 70.1 | 11.0 | 11.0 | 6.24 | 3.43 | 2.0 | 1.9 ^b |
| | | | | | | | | 69.9 | | 10.9 | | 3.37 | | |
| | | | | | | | | | | | | 3.93 | | |
| Percrotonate ^f | C ₉ H ₁₄ O ₃ | 42.5 | 36 | 2 | 0.954 | 1.4414 | 60.73 | 60.4 | 8.91 | 8.61 | 10.11 | 9.72 | 2.0 | 2.04 ^b |
| | | | | | | | | 60.5 | | 8.73 | | 9.98 | | |
| Dipersuccinate | C ₁₇ H ₂₂ O ₅ | 32 | 53-54 ^g | .. | ... | ... | 54.94 | 54.9 | 8.45 | 8.31 | 12.20 | 11.92 | 2.0 | 2.1 ^b |
| | | | | | | | | 54.8 | | 8.49 | | 12.28 | | |
| Diperadipate ^h | C ₁₄ H ₂₀ O ₄ | 49.8 | 42-43 ^g | .. | ... | ... | 57.91 | 57.60 | 9.03 | 8.75 | 11.02 | 10.2 | 2.0 | 1.85 ^b |
| | | | | | | | | 57.80 | | 8.94 | | 11.0 | | |
| Diperphthalate | C ₁₈ H ₂₂ O ₆ | 70.3 | 57-57.5 ⁱ | .. | ... | ... | 61.92 | 61.7 | 7.14 | 6.98 | 10.31 | 11.2 | ... | ... |
| | | | | | | | | 61.5 | | 7.09 | | 11.2 | | |
| | | | | | | | | | | | | 10.6 | | |

^a Palladium was used as catalyst. ^b Platinum was used as catalyst. ^c This perester was distilled in a Hickman type molecular still and the temperature given is the bath temperature. ^d From stearoyl chloride, b. p. 190-191° (20 mm.). ^e From undecylenoyl chloride [English and Velick, *THIS JOURNAL*, **67**, 1413 (1945)], b. p. 102° (2 mm.). A molecular still of the falling film type was used to distill this perester. When this perester was heated for a short time at 130°, it polymerized spontaneously into a white solid insoluble in all of the common organic solvents. ^f From crotonyl chloride, b. p. 123-125°. ^g Recrystallized from olefin-free petroleum ether. ^h From adipyl chloride, b. p. 85-87° (3 mm.). ⁱ Recrystallized from a mixture of 25 parts of ethyl ether and 75 parts of olefin-free petroleum ether.

The peresters thus prepared have unusual

- (1) Present address: Harvard Medical School, Boston, Mass.
- (2) Wieland and Maier, *Ber.*, **64**, 1205 (1931); McAlevy, Ph.D. Thesis, M. I. T., 1934.
- (3) Bayer and Villiger, *Ber.*, **34**, 738 (1901).
- (4) Rieche, "Alkylperoxyde und Ozonide," Theodor Steinkoff, Dresden, 1931, p. 22.
- (5) Medwedewa and Alexejewa, *Ber.*, **65**, 133 (1932).
- (6) Milas and McAlevy, *THIS JOURNAL*, **55**, 349 (1935).
- (7) Criegee, *Ber.*, **77**, 22 (1944).

Experimental

***t*-Butyl Perbenzoate.**—To 387 g. of 60% *t*-butyl hydroperoxide maintained at temperatures between 10 and 20° was added, simultaneously with vigorous stirring in the course of one hour, 329 g. of benzoyl chloride and 566 g. of 30% potassium hydroxide solution. The reaction mixture was stirred overnight, then, [the organic layer separated, washed with 200 cc. of 5% sodium carbonate solution,

- (8) Milas and Marsh, unpublished results.

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}^{20} 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}^{20} 1.087; n_D^{20} 1.5148. These values agree well with those given in the literature.

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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.

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

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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.

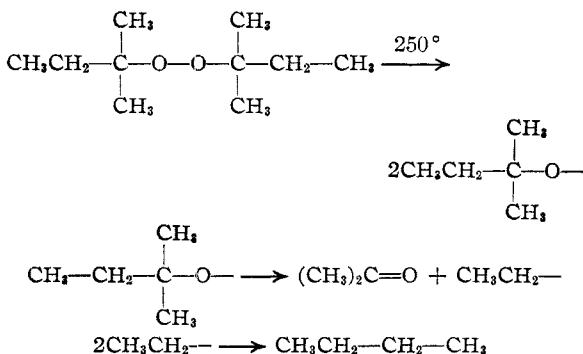
These results seem to indicate that of the three groups attached to the tertiary carbon atom in di-tertiary amyl peroxide, the heavier group splits off preferentially as a free radical which dimerizes to form butane. Additional evidence to support this finding has been produced in the synthesis and pyrolysis of *t*-butyl pentamethyl-ethyl 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}^{20} 0.903; n_D^{20} 1.4161.

Anal. Calcd. for C₅H₁₂O₂: 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



(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).