cyanide. The yields of product are approximately the same or better than can be obtained from lower alkyl sulfonates in the same reaction.

3. Comparison of *n*-butyl methanesulfonate with *n*-butyl *p*-toluenesulfonate has shown that there is no advantage of an ester of an aliphatic sulfonic acid over an ester of an aromatic sulfonic acid for alkylation reactions.

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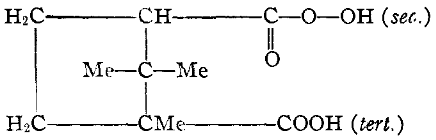
Studies in Organic Peroxides. I. Peroxides in the Camphoric Acid Series

BY NICHOLAS A. MILAS AND AMBROSE MCALEVY

Introduction

In connection with our general studies in auto-oxidation reactions[1] and especially the catalytic effects produced by organic peroxides on these and other related reactions, we had occasion to synthesize and study the properties of several new peroxides. The present communication describes the successful synthesis of some peroxides and peracids which are structurally related to camphoric acid.

A careful search of the literature revealed that up to the present time no definite peroxides of the camphoric acid series have been prepared.[2] We have obtained from camphoric anhydride and sodium peroxide a camphoric acid peracid which has the peracid group attached to the secondary carbon atom.



We have also prepared the methyl ester of this peracid by converting the tertiary monomethyl ester of camphoric acid to the acid chloride, to the ester peroxide and finally to the ester peracid.[3] The possibility of making the isomeric acid peracid through its ester derivative was precluded by the fact that the secondary monomethyl ester yields the tertiary ester secondary acid chloride[4] which gives the same ester peracid obtained from the tertiary monomethyl ester of camphoric acid. This conclusion was

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[1] Milas, THIS JOURNAL, **52**, 739 (1930); **53**, 221 (1931); *Chem. Rev.*, **10**, 295 (1932).

[2] (a) Brodie, *Proc. Roy. Soc.*, (London) **9**, 361 (1858); **12**, 655 (1863); *J. Chem. Soc.*, **17**, 263 (1864); *Ann.* (Supplement), **3**, 217 (1864); (b) Kingzett, *J. Chem. Soc.*, **45**, 93 (1884); (c) Vanino and Thiele, *Ber.*, **29**, 1724 (1896).

[3] Von Baeyer and Villiger, *Ber.*, **33**, 1575 (1900).

[4] Quadrat-J-Khunda, *J. Chem. Soc.*, 208 (1930); Bredt, *J. prakt. Chem.*, **133**, 87 (1932).

verified experimentally. Experiments are being conducted with the monocholesteryl and monoergosteryl esters of camphoric acid to determine the effect of the size of the alcohol group on the migration from the secondary to the tertiary carboxyl.

Experimental Part

_d_-Camphoric Acid Peracid.—To 200 cc. of water at 0° is added with vigorous stirring and cooling during fifteen minutes, 4.3 g. of sodium peroxide, and to this mixture is then added during one hour, 400 cc. of ethyl ether containing 10 g. of *d*-camphoric anhydride (freed from acid by shaking with saturated sodium bicarbonate solution). Stirring is continued for one hour longer, then the ether is removed and 200 cc. of fresh cold ether added. If the peracid is to be used for the estimation of unsaturation, chloroform may be substituted for ether at this stage. The mixture is then acidified in the cold with 25 cc. of 6 *N* sulfuric acid, transferred to a separatory funnel and violently shaken once or twice; the ether layer is separated, shaken with about 100 cc. of saturated ammonium sulfate solution to remove any free hydrogen peroxide present, and dried overnight at 0° with anhydrous sodium sulfate. When the ether is removed at room temperature and under reduced pressure, a highly viscous liquid is obtained having a purity of 87–92% peracid; yield, 6–8 g. A white solid is obtained from the viscous liquid by treating the latter several times with ice-cold low-boiling petroleum ether (freed from unsaturated hydrocarbons) and scratching the vessel with a glass rod. The peracid is finally dried in a vacuum desiccator over concentrated sulfuric acid; m. p. 49–50° (in a sealed tube).

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.53; H, 7.46; active (O), 7.40. Found: C, 55.21; H, 7.45; active (O), 6.93, 7.16, 6.77.

Camphoric acid peracid is soluble in water, and in dilute aqueous solution hydrolyzes to yield camphoric acid and hydrogen peroxide. It is soluble in nearly all organic solvents and slightly soluble in petroleum ether. If kept at 0° and in an atmosphere of dry air, it retains its stability for several weeks. At room temperature camphoric acid peracid decomposes slowly to yield camphoric acid and oxygen, and when heated to 80–100° this reaction proceeds explosively. Its sodium salt reacts in the cold with acid chlorides and anhydrides to give acyl peroxides.

Dicamphoryl Peroxide.—To a mixture of 400 cc. of ethyl ether and 10 g. of *d*-camphoric anhydride is added slowly at 0° with vigorous stirring, a mixture of 50 g. of chopped ice and 2.15 g. of sodium peroxide. After stirring for three-quarters of an hour, the ether is replaced with 400 cc. of fresh ether and the aqueous layer carefully acidified with 6 *N* sulfuric acid. The ether layer, which now contains the peroxide, is removed, dried with anhydrous sodium sulfate and the ether removed in vacuum. The solid which separates out consists of dicamphoryl peroxide and camphoric acid and to remove the latter the solid is extracted several times, each time with a few cc. of anhydrous ethyl ether, the mixture centrifuged and the supernatant ether decanted. Finally the residue is recrystallized several times from an acetone-petroleum ether mixture (4 to 1) and the product dried in a vacuum desiccator over sulfuric acid; m. p. 142° with explosive decomposition; yield of the pure product, 3.4 g.

Anal. Calcd. for $C_{20}H_{30}O_8$: C, 60.28; H, 7.59; active (O), 4.02. Found: C, 60.34, 60.14; H, 7.83, 7.58; active (O), 4.00, 3.92.

The active oxygen was determined in acetone containing sodium iodide and acidified with glacial acetic acid. This peroxide was also obtained in poor yields by the action of camphoric anhydride on the sodium salt of camphoric acid peracid. It is sparingly soluble in water, soluble in acetone and chloroform, somewhat soluble in ether and only slightly soluble in benzene and petroleum ether. It explodes when heated in a flame, producing substances of terpene-like odor.

Camphoryl Tert-monomethyl Ester Sec-chloride.—This chloride was obtained from the *tert.*-monomethyl ester,[5] m. p. 85.4°, and from the *sec.*-monomethyl ester,[5a] m. p. 77°, by the action of phosphorus trichloride in yields of 90%.

Anal. Calcd. for $C_{11}H_{17}O_3Cl$: Cl, 15.42. Found: Cl, 15.60.

Several attempts to distil this acid chloride, even at very low pressures, resulted in its complete decomposition with the formation of camphoric anhydride, dimethyl ester of camphoric acid and hydrogen chloride. Upon hydrolysis it yields *tert.*-monomethyl ester *d*-camphoric acid.[4]

Bis-[tert.-methyl Ester Sec.-camphoryl] Peroxide.—To 80 g. of finely chopped ice is slowly added with shaking 5 g. of sodium peroxide, and to this mixture is added slowly in one hour with continuous shaking 150 cc. of cold ethereal solution containing 10 g. of *tert.*-methyl ester camphoryl chloride. The mixture is violently shaken for half an hour longer to cause the complete conversion of the acid chloride to the peroxide, the ether layer separated, dried by shaking several times with fresh anhydrous sodium sulfate and the ether removed by suction in the cold. The white solid residue is then recrystallized several times from warm low-boiling petroleum ether; m. p. 102°; yield of the pure product, 3.17 g.

Anal. Calcd. for $C_{22}H_{34}O_8$: C, 61.96; H, 7.98; active (O), 3.75. Found: C, 61.52; H, 7.95; active (O) in acetone, 3.52, 3.18.

The above preparation has been repeated using a sample of acid chloride obtained from *sec.*-monomethyl ester *d*-camphoric acid; the same peroxide has been obtained, m. p. 102°. A mixed melting point with the peroxide obtained in the first case showed no depression.

Sec.-methyl Perester Tert.-methyl Camphoric Ester.—This perester is prepared by adding slowly with vigorous stirring to an ice-cold aqueous solution containing the calculated amount of the barium salt of methyl hydroperoxide,[6] 5 g. of *tert.*-methyl ester camphoryl chloride in 200 cc. of ethyl ether. The mixture is shaken at 0° for fifteen minutes longer, the ether layer separated, washed with a saturated solution of sodium bicarbonate, dried with anhydrous sodium sulfate and the ether removed in vacuum; a sirupy liquid is obtained which failed to crystallize.

Anal. Calcd. for $C_{12}H_{20}O_5$: C, 58.99; H, 8.26. Found: C, 58.79; H, 8.50.

Analysis for active oxygen in various solvents yielded rather unsatisfactory results which are in accord with observations of other investigators.[6,7] The perester on standing at room temperature and in the presence of moisture hydrolyzes to yield methyl hydroperoxide and the original monomethyl ester of camphoric acid.

Tert.-methyl Ester Sec.-camphoric Peracid.—To 3 g. of bis-[*tert.*-methyl ester *sec.*-camphoryl] peroxide in 20 cc. of ethyl ether is slowly added at 0° and with vigorous stirring the calculated amount of sodium methylate, and to this mixture is then added 20 cc. of ice water, the mixture well shaken and the ether layer removed. The aqueous layer, which now contains the sodium salt of the peracid, is acidified in the cold with 6 *N* sulfuric acid and the peracid formed extracted with cold ethyl ether, the latter separated, dried over anhydrous sodium sulfate and removed from the peracid by suction at very low pressures. The residue, a highly viscous liquid (1.5 g.), showed distinctly the properties of a peracid, but had a purity of only 50%. Its purity was increased by dissolving the original liquid in pentane, cooling the solution in ice, and subsequently centrifuging

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(5) (a) Walker, *J. Chem. Soc.*, **61**, 1088 (1892); (b) Brühl and Braunschweig, *Ber.*, **25**, 1806 (1892); (c) Haller and Blanc, *Compt. rend.*, **141**, 697 (1905).

(6) Rieche and Hitz, *Ber.*, **62**, 2460 (1929).

(7) Medwedew and Alexejewa, *ibid.*, **65**, 137 (1932).

the suspension formed and rapidly removing it from the supernatant liquid. By repeating this process several times, a product is obtained which has an active oxygen content of 5.44%, corresponding to a purity of 78%. Other methods of purification resulted in the decomposition of the peracid.

The authors take this opportunity to express their gratitude to Prof. James F. Norris for his interest and coöperation.

Summary

1. *d*-Camphoric acid peracid and related peracids and peroxides have been prepared and some of their properties studied.

2. The identity of the acid chlorides obtained from the *sec.*- and *tert.*-monomethyl esters of camphoric acid has been confirmed by conversion into the same ester peroxide.

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Studies in Organic Peroxides. II. The Use of Camphoric Acid Peracid for the Estimation of Unsaturation

BY NICHOLAS A. MILAS AND IVAN S. CLIFF

One of the important reactions of the organic peracids is their reactivity with unsaturated groups, but more particularly with substances containing double bonds. This reaction has been studied by various investigators,[1] but cannot be generalized since it depends not only upon the reactivity of the unsaturated group which is usually governed by the adjacent groups attached to the latter,[2] but also upon the activity of the peracid itself. Furoic peracid, for example, is far more reactive than benzoperacid or camphoric acid peracid, while phthalic acid peracid fails completely to add to many unsaturated compounds.[3] Although numerous abnormalities have been reported[4] with benzoperacid and aceto-

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[1] (a) Prileschajew, *Ber.*, **42**, 4811 (1909). (b) Bergmann and co-workers, *ibid.*, **54**, 440 (1921); **56**, 2255 (1923); *Ann.*, **432**, 333 (1923). (c) Derx, *Rec. trav. chim.*, **41**, 332 (1922); (d) Hibbert and Burt, THIS JOURNAL, **47**, 2240 (1925); (e) Bauer and Kutscher, *J. prakt. Chem.*, **122**, 201 (1929); Nametkin and Brüssov, *ibid.*, **112**, 169 (1926); **115**, 56 (1927). (f) Böeseken and co-workers, *Rec. trav. chim.*, **44**, 90 (1925); **47**, 683 (1928); **49**, 95 (1930); *J. prakt. Chem.*, **131**, 285 (1931); (g) Pummerer and co-workers, *Ber.*, **62**, 1411 (1929).

[2] Meerwein and co-workers, *J. prakt. Chem.*, **113**, 9 (1926); Böeseken and Blumberger, *Rec. trav. chim.*, **45**, 838 (1926); Charrier and Moggi, *Gazz. chim. ital.*, **57**, 736 (1928); Smit, *Rec. trav. chim.*, **49**, 675, 691 (1930).

[3] Milas and McAlevy, unpublished results.

[4] Arbuzov and Mikhailov, *J. prakt. Chem.*, **127**, 1, 92 (1930); Bodendorf, *Arch. Pharm.*, **268**, 491 (1930).