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).

peracid, these peracids are the only ones used extensively for the quantitative estimation of the double bond.

The recent synthesis[5] of camphoric acid peracid suggested its use as a reagent for the estimation of unsaturation and for the preparation of oxides and glycols from the corresponding ethylenic compounds. The present communication, therefore, deals with some of the quantitative results obtained with several unsaturated compounds chosen from various branches of organic chemistry. Because of its comparative ease of preparation, camphoric acid peracid may prove a more desirable reagent than benzoperacid.

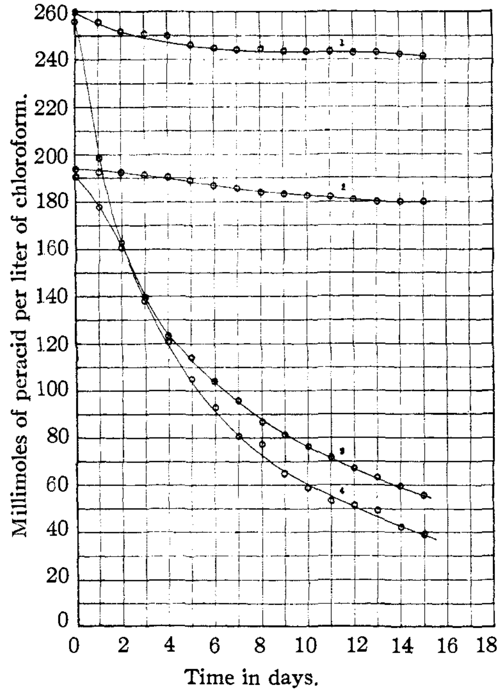

Fig. 1.—The stability of benzoperacid and camphoric acid peracid in chloroform: Curve 1, benzoperacid in chloroform at 0°; Curve 2, camphoric acid peracid in chloroform at 0°; Curve 3, camphoric acid peracid in chloroform at 25°; Curve 4, benzoperacid in chloroform at 25°.

The stability of camphoric acid peracid and that of benzoperacid has been determined quantitatively in chloroform solution at 0° and at 25° and the results are plotted in Fig. 1. Both peracids were prepared at the same time and their chloroform solutions dried with anhydrous sodium sulfate to exactly the same extent, *e. g.*, shaken twice each time with fresh anhydrous sodium sulfate, then allowed to stand over this reagent for twenty-four hours at 0°. Each solution was then filtered and divided into two portions, one kept at 0° and the other at 25°. To determine the concentration of peracid in each solution, 1-cc. portions were pipetted from time to time and titrated in the usual manner against standard sodium thiosulfate solution. The concentration of each peracid expressed in millimoles per liter of chloroform solution is plotted in Fig. 1 against time. The results seem to indicate clearly that camphoric acid peracid is slightly more stable at 0° but decidedly more stable at 25° than benzoperacid.

Quantitative Estimation of Unsaturation.—All unsaturated substances used in this investigation were of the purest quality obtainable and in cases of doubtful purity

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[5] Milas and McAlevy, THIS JOURNAL, 55, 349 (1933).

each compound was carefully purified and its constants determined. The procedure adopted for the determination of unsaturation consists in mixing a weighed amount of the unsaturated substance with an excess amount of peracid in chloroform solution and allowing the mixture to stand at room temperature for one-half hour; the excess peracid is then titrated in the usual manner. The results are given in Table I in which the theoretical and observed values are expressed in moles of camphoric acid peracid required and moles actually used. It may be seen from this table that camphoric acid peracid could be successfully used with several substances for the quantitative estimation of unsaturation. Similar exceptions to those recorded in this table have been observed by Böeseken[2] and others with benzoperacid and acetoperacid.

TABLE I

THE USE OF CAMPHORIC ACID PERACID FOR THE ESTIMATION OF UNSATURATION

Substance	No. of double bonds	Moles of peracid consumed[a]	Remarks
Anethole	1	0.983	
Isosafrole	1	.979	
Isoeugenol	1	.981	
Citronellol	1	.983	
Cholesterol	1	.980	
Ergosterol	3	2.994	
Limonene	2	1.957	
d-Pinene	1	1.010	
Nonene	1	0.947	
2,4-Dimethylpentene-2	1	.972	
2,4-Hexadiene	2	.923	Only one C=C reacted
2,4-Hexadiene	2	.993	34 hours at 0°
Oleic acid	1	.997	34 hours at 0°
Linoleic acid	2	2.026	34 hours at 0°
Cinnamic acid	1	...	No measurable amount in one hour
Cinnamic aldehyde	1	0.57	34 hours at 0°
Abietic acid	1	.84	34 hours at 0°
Crotonic acid	1	.15	5 hours at room temperature
Mesityl oxide	1	.49	5 hours at room temperature

[a] Average of at least two determinations.

Isolation of Products Formed by the Interaction of Camphoric Acid Peracid with Unsaturated Compounds. ***d*-Pinene Oxide.**—Five grams of *d*-pinene was mixed with a large excess of camphoric acid peracid in chloroform and the mixture was allowed to stand at 0° for three days. It was then shaken with a 10% solution of sodium hydroxide to remove the unused peracid and camphoric acid, and finally washed with water and dried over anhydrous sodium sulfate for twenty-four hours. The chloroform solution was then removed by distillation and the remaining liquid subjected to fractional distillation under reduced pressure; the fraction distilling at 102–103° (50 mm.) was collected and its physical constants determined.

TABLE II

PHYSICAL CONSTANTS OF THE PRODUCT BOILING AT 102–103° (50 MM.)

	Pinene oxide[1a] (Prileschajew)	Our product
B. p. (50 mm.)	102–103°	102–103°
d_{16}^{16}	0.9689	0.9675
n_{D}^{16}	1.4708	1.4740

Cholesterol Oxide.—Eight-tenths of a gram of cholesterol (Eastman Kodak C. P. product) was mixed with a large excess of camphoric acid peracid in 200 cc. of chloroform and the mixture allowed to stand at 0° for five days. The mixture was then shaken twice, each time with 200 cc. of 1 *N* sodium hydroxide solution, then with water and dried over calcium chloride. It was filtered and the chloroform removed by distillation. The residue, a white solid (m. p. 125–130°), was recrystallized three times from ethyl acetate, giving a constant melting point of 141–142°. Westphalen[6] gives a melting point of 140–141° for cholesterol oxide.

Hydrolysis of Cholesterol Oxide.—To prove definitely that our product was the oxide, 0.4 g. of the latter was heated with 4 cc. of water in a sealed tube at 115° for twelve hours. The resulting white solid was recrystallized twice from ethyl alcohol, m. p. 239.3°. The melting point of cholestantriol has been reported by Pickard and Yates[7] and by Westphalen[6] to be 239°.

Summary

1. The stability of camphoric acid peracid and benzoperacid, in chloroform, has been measured at 0° and at 25°.

2. At 25° camphoric acid peracid is more stable, in chloroform solution, than benzoperacid, while at 0° the difference in stability is not significant.

3. Camphoric acid peracid was found to add quantitatively to certain types of unsaturated substances.

4. Pinene and cholesterol oxides have been definitely isolated from the interaction of camphoric acid peracid and *d*-pinene and cholesterol.

[6] Westphalen, *Ber.*, **48**, 1064 (1915).

[7] Pickard and Yates, *J. Chem. Soc.*, **93**, 1684 (1908).

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The Action of Sodium Alcoholate and of Sodium Amalgam on Aromatic Pinacols

BY W. E. BACHMANN

Reaction of Pinacols with Sodium Alcoholate.—According to Schlenk and Thal[1] sodium ketyl radicals are formed when a suspension of benzopinacol in alcohol is treated with a concentrated alcoholic solution of sodium alcoholate. We found, in agreement with Schlenk and Thal, that the deep blue color of the ketyl is produced in the reaction, but we observed further that the color disappeared completely after a short time. At first this disappearance of color was attributed to oxidation of the ketyl by oxygen of the air. That this was not the case was definitely proved when the same disappearance of color occurred when air was excluded. Hydrolysis of the colorless solution gave a mixture of equal parts of benzophenone and benzohydrol.

[1] Schlenk and Thal, *Ber.*, **46**, 2841 (1913).