method,[3] may be compared with that of 7.78 × 10^{-6} sec.$^{-1}$ at 24.85°, determined by conductivity.[4]

By suitable extraction techniques, this method may be used also for reactions in solvents that absorb in this region. Thus, reactions of methyl tosylate in benzene can be followed by extracting aliquots of the reaction mixture with water, back-extracting with cyclohexane, and measuring the absorbance of the water layer. In a number of runs in water, methyl tosylate was determined in cyclohexane after extraction. Similarly, extraction techniques may also be devised for following the reactions of an ester whose absorption is the same as that of the anion produced.

Experimental

The procedure used for the reactions in water is described below using the hydrolysis of methyl tosylate as a typical example.

Water was laboratory distilled water redistilled from sodium hydroxide–potassium permanganate in an all-Pyrex apparatus. It was degassed by bubbling carbon dioxide-free nitrogen through it for at least 20 min.

Methyl tosylate, Eastman White Label grade, was recrystallized from reagent grade cyclohexane–ether and dried in a desiccator over phosphorus pentoxide at 22° (1 mm.) for 3 days. The ester was allowed to melt, cooled, and a seed crystal was introduced. When approximately 75% of the material had crystallized, the solid ester was collected on a filter and then dried as before for 24 hr. The methyl tosylate, m.p. 28.4–29.4° (uncor.) lit.[5] m.p. 28–29°, was stored in a desiccator over Drierite (calcium sulfate).

Kinetics.—Temperature control was ± 0.02°. The temperature was determined using a thermometer calibrated by the National Bureau of Standards.

A 50-ml. volumetric flask was filled to the mark with water under an atmosphere of carbon dioxide-free nitrogen. Approximately 10 μl. of methyl tosylate was added and the resulting mixture was shaken vigorously to give the reaction solution, which was placed in the constant-temperature bath at 25°. After 10 min. (zero point), and at suitable times thereafter, a sample of reaction solution was transferred to a glass-stoppered 1-cm. silica cell and its absorbance was determined at 261 mμ at a slit width of 0.4 mm. using a Beckman DU spectrophotometer. A Beer's law plot (absorbance *vs.* fraction sodium tosylate) was linear for the change from methyl tosylate to tosylate anion. The concentration of methyl tosylate present initially was calculated from the infinity point, which was taken after the solution had been in the bath for 10 half-lives.

First-order rate constants were obtained from a plot of per cent unchanged methyl tosylate *vs.* time on semilogarithmic paper by dividing 0.693 by the half-life. Data for a typical run are shown in Table I.

TABLE I
HYDROLYSIS OF 1.22 × 10^{-3} *M* METHYL TOSYLATE IN WATER AT 25°

Time, hr.	Absorbance	% unchanged
0.0	0.791	100.0
5.0	0.746	87.9
9.0	0.709	77.9
18.0	0.645	60.6
24.0	0.611	51.5
32.0	0.570	40.4
44.0	0.526	28.6
55.0	0.498	21.0
67.0	0.471	13.7
290.0	0.420	0.0

$k_1 = 7.91 \times 10^{-6}$ sec.$^{-1}$

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(3) C. R. Morgan, Ph.D. thesis in Organic Chemistry, Massachusetts Institute of Technology, May, 1963, p. 49.

(4) R. E. Robertson, *Can. J. Chem.*, **33**, 1536 (1955).

(5) F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 460 (1951).

α-Pinene Oxide Reaction with Acetic Acid–Sodium Acetate

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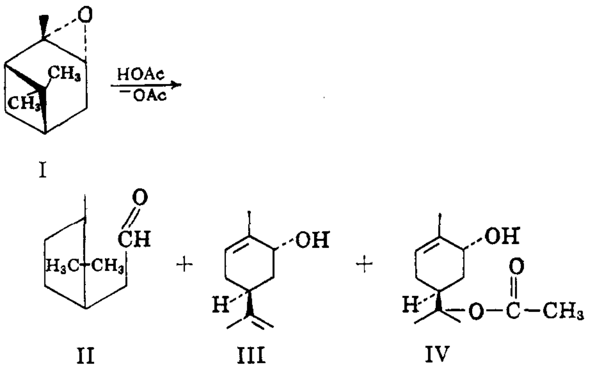
In a previous study,[3] the reaction of α-pinene oxide (I) with glacial acetic acid was reported to give campholenaldehyde (II) and a high boiling fraction which was apparently a crude hydroxyacetate. Arbuzow and Mikhailow[4] have reported the formation of a glycol monoacetate on treatment of α-pinene with peracetic acid in chloroform solution, and that a similar product was obtained on treatment of α-pinene oxide with acetic acid.

We have reinvestigated the reaction of *dl*-α-pinene oxide with a solution of sodium acetate in glacial acetic acid and found it to afford 39% campholenaldehyde, 19% *dl-trans*-carveol (III), and 23% *dl-trans*-8-acetoxy-6-hydroxy-1-*p*-menthene (IV). Identity of the latter product was established by saponification to *dl-trans*-sobrerol, and by pyrolysis to yield *dl-trans*-carveol (III) as the only product.

Inasmuch as the conversion of α-pinene oxide in this and previously reported work[4–7] to sobrerol or its derivatives has invariably afforded the *trans* isomers,[8] the stereochemistry of the epoxide must be as shown in I, the influence of steric hindrance playing a role similar to that observed for pinol.[9]

In view of the present results, the theoretical arguments of Brewster,[10] and the hydrogenation of the higher rotating carvotanacetol to the carvomenthols having the hydroxyl *trans* to the isopropyl group,[11] we must conclude that the generally accepted con-



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[1] Research Associate, Newport Industries Division, Heyden Newport Chemical Corp., Pensacola, Fla.

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[3] E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955); L. C. King and H. Farber, *J. Org. Chem.*, **26**, 326 (1961).

[4] B. A. Arbuzow and B. M. Mikhailow, *J. prakt. Chem.*, **127**, 1 (1930).

[5] N. Prileschaev and V. Vershuk, *J. Russ. Phys. Chem. Soc.*, **67**, 473 (1929).

[6] A. J. Durbetaki and S. M. Linder, U. S. Patent 2,949,489 (1960); *Chem. Abstr.*, **55**, 608 (1961).

[7] E. A. Klein, U. S. Patent 2,815,378 (1957).

[8] H. Schmidt, *Ber.*, **86**, 1437 (1953).

[9] K. Piatkowski and H. Kuczynski, *Roczniki Chem.*, **35**, 1579 (1961).

[10] J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5493 (1959), and references therein.

[11] R. L. Kenney and G. S. Fisher, *J. Org. Chem.*, **28**, 3509 (1963).

figurational assignments for the carveols are correct, and that the reassignments suggested by Farges and Kergomard[12] are invalid.

Experimental

Melting points were taken in capillaries on a Mel-Temp melting point apparatus and are uncorrected. Boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 21 recording spectrophotometer. Gas–liquid chromatography separations were effected on a Wilkins Aerograph Master Model A-100 equipped with a 10-ft., 0.25-in., Carbowax 20 M column. Analyses were by G. Weiler and F. B. Strauss, Oxford, England.

Reaction of *dl*-α-Pinene Oxide with a Sodium Acetate–Glacial Acetic Acid Solution.—Freshly distilled *dl*-α-pinene oxide (136 g.), b.p. 63–65° (10 mm.), n^{25}_{D} 1.4670, was slowly added to a slurry of sodium acetate (123 g.) in glacial acetic acid (600 g.) over a period of 2.5 hr. The reaction temperature rose to approximately 40°. The reaction was stirred for 72 hr., during which time the temperature dropped to 27°. The reaction mixture was poured into 1000 ml. of water, the oil layer separated, and the aqueous phase extracted with three 100-ml. portions of ether. The organic phases were combined, neutralized with a saturated sodium bicarbonate solution, and washed with three 75-ml. portions of water. The ethereal phase was dried over anhydrous sodium sulfate. The ether was removed under reduced pressure and the product distilled over a 3-ft. spinning band column to give three fractions. The first fraction (53 g.) was campholenaldehyde (39%), b.p. 80° (10 mm.), n^{25}_{D} 1.4630, which gave a yellow 2,4-DNP, m.p. 110–111°, and semicarbazone, m.p. 138.5–140° (lit.[3] m.p. 139.5–140.5°).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.61; H, 10.63.

The second component (26 g.), b.p. 76° (4 mm.), n^{25}_{D} 1.4949, was identified as *dl-trans*-carveol (19.1%) by g.l.c. and infrared comparison with an authentic sample of *d-trans*-carveol. This alcohol formed a 3,5-dinitrobenzoate, m.p. 118–118.5° (lit.[13] n^{19}_{D} 1.4956, 3,5-dinitrobenzoate m.p. 119°).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.48; H, 10.55.

The third component (43.5 g.), b.p. 128–133° (4 mm.), n^{25}_{D} 1.4813, was subsequently identified as the monoacetate of sobrerol (*dl-trans*-8-acetoxy-6-hydroxy-1-*p*-menthene, 22.9%), which gave a 3,5-dinitrobenzoate, m.p. 130.5–132°.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.24; H, 9.72.

Saponification of the hydroxyacetate (0.4 g.) with a solution of 4 ml. of 50% potassium hydroxide in 10 ml. of a 20% ethanol solution afforded *dl-trans*-sobrerol, m.p. 128–129°, whose melting point was undepressed on admixture with an authentic sample.[6]

Pyrolysis of *dl-trans*-8-Acetoxy-6-hydroxy-1-*p*-menthene.—The sobrerol monoacetate (6.0 g.), produced above, was pyrolyzed at 370°. The pyrolysis product was taken up in ether, neutralized with a sodium bicarbonate solution, washed with water, and dried over anhydrous sodium sulfate. After removal of the solvent, the crude product (4.24 g.), identified by g.l.c. to be greater than 90% *trans*-carveol, was distilled on a modified Hickman still to give *dl-trans*-carveol (3.78 g.), n^{25}_{D} 1.4959, 3,5-dinitrobenzoate m.p. 119°. This alcohol gave an infrared spectrum identical with an authentic sample.

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[12] G. Farges and A. Kergomard, *Bull. soc. chim. France*, 51 (1963).

[13] E. Guenther and D. Althausen, "The Essential Oils," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 203.

An Improved Synthesis of Peroxybenzoic Acid

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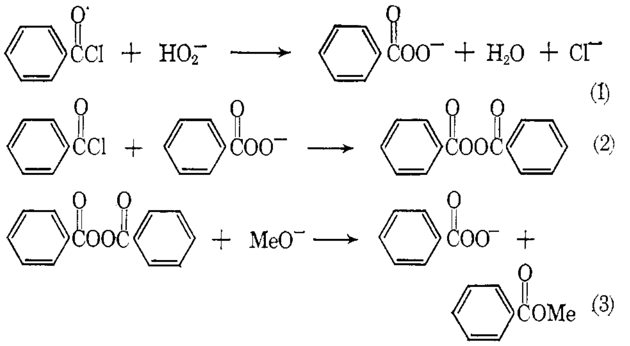
Peroxybenzoic acid is commonly prepared by a two-step process. In the first step, benzoyl chloride reacts with aqueous sodium peroxide. Because benzoyl chloride is immiscible with the solution, the reaction with the hydroperoxide ion (eq. 1) takes place at the surface of the droplets. The peroxybenzoate anion is less reactive toward benzoyl chloride than is HO_2^-, but reacts preferentially (eq. 2) because it is in contact. Several experimental procedures have been given.[1-3]

In the second step, benzoyl peroxide is cleaved by sodium methoxide (eq. 3). The procedure described by Braun[4] has been modified by later workers.[5,6]



Kergomard and Bigou[7,8] and Vilkas[9] have reported a method which avoids the formation of benzoyl peroxide. Sodium peroxide, or equivalent amounts of hydrogen peroxide and sodium hydroxide, is dissolved in a mixed solvent system in which benzoyl chloride is also soluble. In such a system, the peroxybenzoate ion and the hydroperoxide ion can compete as nucleophiles for benzoyl chloride. Very little benzoyl peroxide is formed. Peroxybenzoic acid can be recovered from the reaction mixture as soon as the addition of benzoyl chloride is complete.

This method is quicker, gives better yields, and is much safer in that neither benzoyl peroxide nor sodium metal is involved. It has the disadvantage of requiring a reaction temperature of −5° or lower.

We have had occasion to repeat many times this last method. We consistently obtain better yields using sodium peroxide rather than hydrogen peroxide and sodium hydroxide. Purification of the sodium peroxide by recrystallization as $Na_2O_2 \cdot 8H_2O$ gives further improvements in yield. This indicates that catalytic decomposition is occurring.

In commercial bleaching operations, the catalytic effect of traces of metal ions is inhibited by adding a small amount of magnesium sulfate.[10] We have found that the addition of a little magnesium sulfate to the reaction mixture allows the reaction to be run at room

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[1] C. C. Price and E. Krebs, *Org. Syn.*, **23**, 65 (1943).

[2] C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5432 (1950).

[3] J. D'Ans, J. Mattner, and W. Busse, *Angew. Chem.*, **65**, 57 (1953).

[4] G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.

[5] I. M. Kolthoff, T. S. Lee, and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).

[6] C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4250 (1953).

[7] A. Kergomard and J. Bigou, *Bull. soc. chim. France*, 486 (1956).

[8] A. Kergomard and J. Bigou, *ibid.*, 334 (1958).

[9] M. Vilkas, *ibid.*, 1501, (1959); French Patent 1,177,466 (1958).

[10] L. A. Beeman and J. S. Reichert, "The Bleaching of Pulp," R. S. Hatch, Ed., Technical Association of the Pulp and Paper Industry, New York, N. Y., 1953, p. 228.