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CHAPTER 7

EPOXIDATION AND HYDROXYLATION OF ETHYLENIC COMPOUNDS WITH ORGANIC PERACIDS

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CONTENTS

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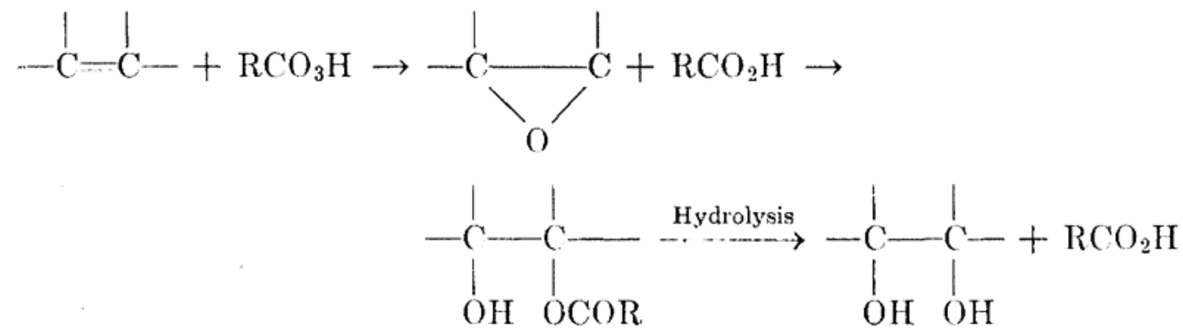
INTRODUCTION

Oxiranes (α-epoxy compounds) and α-glycols can be prepared from olefins by a variety of methods. One of the most important and most generally applicable of these is the oxidation of ethylenic compounds with organic peracids, as exemplified by the accompanying equations.



Depending upon the peracid employed and/or the operating conditions, either an oxirane [1,2,3] or an α-glycol [2,4] can be obtained in good yield. Ordinarily the oxirane isolated can be hydrolyzed to the α-glycol.[5] It is important to note that the oxidation step both in epoxidation and hydroxylation reactions with organic peracids is the conversion of the olefin to the oxirane.

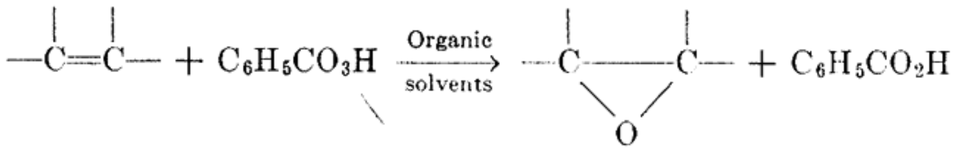
The literature on the epoxidation and hydroxylation of compounds containing an isolated ethylenic linkage is so extensive that no attempt has been made to include conjugated systems in a comprehensive fashion. However, occasional comments on α,β-unsaturated acids are found on pp. 385 and 388, the preferential epoxidation of one ethylenic linkage in isoprene is described on p. 397, and a limited number of conjugated dienes and α,β-unsaturated acids are included in Table I.

[1] Findley, Swern, and Scanlan, *J. Am. Chem. Soc.*, **67**, 412 (1945).
[2] Swern, Billen, and Scanlan, *J. Am. Chem. Soc.*, **68**, 1504 (1946).
[3] Swern, Findley, and Scanlan, *J. Am. Chem. Soc.*, **66**, 1925 (1944).
[4] Swern, Billen, Findley, and Scanlan, *J. Am. Chem. Soc.*, **67**, 1786 (1945).
[5] Swern, *J. Am. Chem. Soc.*, **70**, 1235 (1948).

SCOPE

Epoxidation

Perbenzoic Acid. The discovery that oxiranes can be prepared from ethylenic compounds by epoxidation with an organic peracid is generally credited to the Russian chemist, Prileschajew,[6-9] who showed that perbenzoic acid is an efficient oxidizing agent for the epoxidation of isolated double bonds. This reaction is excellent for preparative pur-



poses. It proceeds under mild conditions, and it is generally conducted in a non-reactive organic solvent, such as chloroform, ether, benzene, acetone or dioxane. The reaction time is usually short, but it varies with the number and nature of the groups attached to the ethylenic system.[10] As a rule the yields are high.

Most investigators have preferred to prepare a solution of perbenzoic acid [3,11-15] for epoxidation. However, since perbenzoic acid can be prepared conveniently by the oxidation of benzaldehyde with oxygen,[3,16-19] some investigators have treated solutions of benzaldehyde and the unsaturated compound with air or oxygen, the perbenzoic acid being consumed as it is formed. This application of the perbenzoic acid epoxidation technique, in which separate preparation and isolation of the peracid is avoided, has been applied to the oxidation of methyl oleate,[20] oleyl alcohol,[20] octenes,[21] oleic acid,[3,22] stilbene,[22] styrene,[22] and squalene,[22] and good yields of oxiranes were generally obtained. When

[6] Prileschajew, *Ber.*, **42,** 4811 (1909).
[7] Prileschajew, *J. Russ. Phys. Chem. Soc.*, **42,** 1387 (1910) [*J. Chem. Soc. Abstr.*, **100, I,** 255 (1910)].
[8] Prileschajew, *J. Russ. Phys. Chem. Soc.*, **43,** 609 (1911) [*C. A.*, **6,** 348 (1912)].
[9] Prileschajew, *J. Russ. Phys. Chem. Soc.*, **44,** 613 (1912) [*C. A.*, **6,** 2407 (1912)].
[10] Swern, *J. Am. Chem. Soc.*, **69,** 1692 (1947).
[11] Braun, *Org. Syntheses, Coll. Vol.* **1,** 431, 2nd ed. (1941).
[12] Hibbert and Burt, *J. Am. Chem. Soc.*, **47,** 2240 (1925).
[13] Kolthoff, Lee, and Mairs, *J. Polymer Sci.*, **2,** 199 (1947).
[14] Levy and Lagrave, *Bull. soc. chim. France*, [4] **37,** 1597 (1925).
[15] Tiffeneau, *Org. Syntheses*, **8,** 30 (1928).
[16] Jorissen and van der Beek, *Rec. trav. chim.*, **45,** 245 (1926).
[17] Jorissen and van der Beek, *Rec. trav. chim.*, **46,** 42 (1927).
[18] Jorissen and van der Beek, *Rec. trav. chim.*, **49,** 138 (1930).
[19] van der Beek, *Rec. trav. chim.*, **47,** 286 (1928).
[20] Swern and Findley, *J. Am. Chem. Soc.*, **72,** 4315 (1950).
[21] Pigulevskii, *J. Gen. Chem.* (*U.S.S.R.*), **4,** 616 (1934) [*C. A.*, **29,** 2145 (1935)].
[22] Raymond, *J. chim. phys.*, **28,** 480 (1931).

aliphatic aldehydes, such as acetaldehyde and butyraldehyde, are employed instead of benzaldehyde, poor yields of oxiranes result.[20,21,23]

Epoxidation with perbenzoic acid has been employed in the preparation of oxiranes from an extremely large number and wide variety of ethylenic compounds (see Table I).

Monoperphthalic Acid. Another reagent that has been employed in the preparation of oxiranes is monoperphthalic acid; but this reagent, although efficient, has not been studied so extensively as perbenzoic acid, primarily because it offers only minor advantages in most reactions. When the epoxidation requires a long period of time for completion, however, the greater stability of monoperphthalic acid,[24,25] compared to perbenzoic acid, is an advantage. Furthermore, since epoxidations with monoperphthalic acid are usually conducted in chloroform solution and the phthalic acid formed is insoluble, it is readily separated from the oxidation product. Although Böhme [26,27] was apparently the first to demonstrate that monoperphthalic acid is consumed by reaction with the ethylenic linkage, Chakravorty and Levin [25] were the first to isolate oxiranes by the oxidation of unsaturated compounds with this oxidizing agent. Epoxidation with monoperphthalic acid is conducted under the same conditions as with perbenzoic acid, and good yields of oxiranes are obtained. Epoxidation with monoperphthalic acid has been applied most extensively to naturally occurring products, such as sterols and polyenes. Ethylenic compounds which have been converted to oxiranes by epoxidation with monoperphthalic acid are listed in Table I.

Peracetic Acid. Since peracetic acid is one of the most conveniently prepared organic peracids, a study of its possible use as an epoxidizing agent was to be expected. For a long time, however, it was assumed that oxiranes could not be prepared by the epoxidation of olefins with peracetic acid since the products isolated from such reactions were either α-glycols or their monoacetates. The first successful epoxidation with peracetic acid was reported by Böeseken, Smit, and Gaster,[28,29] who obtained methyl 9,10,12,13-diepoxystearate from methyl linoleate, but the yields were extremely poor and the major proportion of the product consisted of a polymer of undetermined constitution.[30] In a systematic study of the reaction of unsaturated compounds with peracetic acid in

[23] Findley and Swern, U. S. pat. 2,567,930 [*C. A.*, **46,** 3560 (1952)].
[24] Baeyer and Villiger, *Ber.*, **34,** 762 (1901).
[25] Chakravorty and Levin, *J. Am. Chem. Soc.*, **64,** 2317 (1942).
[26] Böhme, *Ber.*, **70,** 379 (1937).
[27] Böhme and Steinke, *Ber.*, **70,** 1709 (1937).
[28] Böeseken, Smit, and Gaster, *Proc. Acad. Sci. Amsterdam*, **32,** 377 (1929).
[29] Smit, *Rec. trav. chim.*, **49,** 675 (1930).
[30] Swern, unpublished results.

acetic acid solution and in inert solvents, Arbusow and Michailow [31,32] observed that hydroxy acetates were formed in acetic acid while good yields of oxiranes were obtained in inert solvents. They concluded that the behavior of peracetic acid toward olefins is the same as that of perbenzoic acid, but that when an acetic acid solution is employed the oxirane is converted to the hydroxy acetate by further reaction with acetic acid. The apparent necessity for employing peracetic acid in an inert solvent to obtain good yields of oxiranes discouraged the general use of peracetic acid for epoxidation, because peracetic acid can be prepared and used most conveniently in acetic acid, whereas its isolation free (or substantially free) of acetic acid is time-consuming and hazardous.

Subsequently, however, in connection with a kinetic study of the reaction of peracetic acid in acetic acid solution with various long-chain olefins, suitable reaction conditions were determined for the efficient conversion of ethylenic compounds to oxiranes.[1] To obtain good yields of oxiranes it is necessary to operate at moderate temperatures (20–25° is preferred), to keep the reaction time as short as possible and to exclude strong acids, which catalyze the opening of the oxirane ring by acetic acid. The reaction was shown to be general and afforded a simple and convenient method for the preparation of oxirane compounds in quantity. Isolation of pure peracetic acid and employment of inert solvents were unnecessary. Yields of oxiranes, however, were usually lower than when perbenzoic or monoperphthalic acid was employed. In the peracetic acid epoxidation of compounds containing both an ethylenic and an acetylenic linkage, it has been reported that only the double bond is attacked.[33,34] Acetylenic compounds react with peracetic acid, but the rates of reaction are only about one-thousandth as great as the rates of reaction of analogous ethylenic compounds. Three atoms of oxygen add, and the acetylenic linkage is cleaved. Oxirenes, —C≡≡≡C—, are

intermediates and have been isolated from some reactions.[34a]

Ethylenic compounds which have been converted to oxiranes by epoxidation with peracetic acid are listed in Table I.

Percamphoric Acid. Percamphoric acid has been employed to convert pinene and cholesterol to the corresponding oxiranes.[35]

[31] Arbusow and Michailow, *J. prakt. Chem.*, **127**, 1 (1930).
[32] Arbusow and Michailow, *J. prakt. Chem.*, **127**, 92 (1930).
[33] Malenok and Sologub, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 150 (1940) [*C. A.*, **34**, 7286 (1940)].
[34] Malenok and Sologub, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 983 (1941) [*C. A.*, **37**, 355 (1943)].
[34a] Schlubach and Franzen, *Ann.*, **577**, 60 (1952).
[35] Milas and Cliff, *J. Am. Chem. Soc.*, **55**, 352 (1933).

Performic Acid. Performic acid is generally considered not to be an epoxidation reagent because the high acidity of formic acid (employed either as solvent or formed in the oxidation) causes most oxirane rings to open rapidly. It has been shown recently, however, that α-diisobutylene yields an isolable oxirane on oxidation with performic acid, although the yield is low.[36] By employing only small quantities of formic acid as solvent and oxygen carrier, and in some cases by adding small amounts of sodium hydroxide, it has been reported that methyl oleate, octyl oleate, propylene glycol dioleate, and soybean oil can be converted to oxiranes in fair yields.[37] Recently, two steroids have been converted to oxiranes by epoxidation with performic acid.[38,39]

The diisobutylenes behave somewhat abnormally on reaction with both performic and peracetic acids, yielding, besides the expected products, unsaturated alcohols, an aldehyde, a ketone, a cyclic diether, and high-boiling products.[36,40–43]

Hydroxylation

Peracetic Acid. The use of peracetic acid for the preparation of α-glycols from unsaturated substances probably exceeds that of all other organic peracids combined. Peracetic acid is usually prepared and employed in either of two ways: (1) the peracid is preformed by the reaction of acetic acid or acetic anhydride with 25–90% hydrogen peroxide [1,44–47] and then mixed with the unsaturated compound, or (2) the unsaturated compound is mixed with hydrogen peroxide and acetic acid, and the peracetic acid is consumed as it is formed.[4,48] Under suitable conditions (p. 381) oxiranes are obtained in good yields; but in the manner that the reactions have usually been carried out (long reaction times, and/or high temperatures, and/or in the presence of sulfuric acid), the products isolated are hydroxy acetates formed by the reaction of excess acetic acid with the oxirane produced initially. The hydroxy

[36] Byers and Hickinbottom, *J. Chem. Soc.*, **1948**, 1328.
[37] Niederhauser and Koroly, U. S. pat. 2,485,160 [*C. A.*, **44**, 7346 (1950)].
[38] Djerassi, Mancera, Stork, and Rosenkranz, *J. Am. Chem. Soc.*, **73**, 4496 (1951).
[39] Stork, Romo, Rosenkranz, and Djerassi, *J. Am. Chem. Soc.*, **73**, 3546 (1951).
[40] Byers and Hickinbottom, *J. Chem. Soc.*, **1948**, 284.
[41] Byers and Hickinbottom, *Nature*, **158**, 341 (1946).
[42] Hickinbottom, *J. Chem. Soc.*, **1948**, 1331.
[43] Hickinbottom, *Nature*, **159**, 844 (1947).
[44] D'Ans and Frey, *Ber.*, **45**, 1845 (1912).
[45] D'Ans and Frey, *Z. anorg. Chem.*, **84**, 145 (1914).
[46] D'Ans and Kneip, *Ber.*, **48**, 1136 (1915).
[47] Greenspan, *J. Am. Chem. Soc.*, **68**, 907 (1946).
[48] Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947).

acetates are readily hydrolyzable to α-glycols in excellent yield.[49-52] Although good yields of glycols were reported by some early investigators, the operating conditions employed caused the loss of much active oxygen by decomposition. With sulfuric acid as the catalyst, moderate temperatures (40°), and short reaction periods, excellent yields of α-glycols are obtained with stoichiometric quantities of 25–30% hydrogen peroxide.[4] Since the sulfuric acid catalyzes the formation of peracetic acid and the peracid is rapidly consumed at 40°, the reaction is complete in a few hours and little active oxygen is lost. This procedure is one of the most efficient for converting long-chain olefins to α-glycols. Slightly higher yields of α-glycols are obtained when 90% hydrogen peroxide is employed.[48]

Ethylenic compounds which have been converted to α-glycols by oxidation with peracetic acid, either preformed or prepared and utilized *in situ*, are listed in Table I. Some of the unsaturated substances listed have been converted to hydroxy acetates rather than to α-glycols, but the conversion to glycols is effected so readily by hydrolysis that these substances have also been included.

Performic Acid. An even more efficient and rapid hydroxylation technique consists in the reaction of unsaturated compounds with performic acid.[4] Not only is performic acid formed rapidly when 25–90% hydrogen peroxide and formic acid are mixed,[44-47, 53] but it also reacts rapidly and completely with the unsaturated linkage. By means of this hydroxylation reaction, conversion of an unsaturated compound to an α-glycol is accomplished within a short time, and approximately stoichiometric quantities of hydrogen peroxide can be employed. The initial product of oxidation is not the α-glycol but the oxirane, which is rapidly converted in most cases to a hydroxy formate as a result of the high acidity of formic acid. Hydroxy formates are the products usually isolated and are readily converted to the α-glycols by hydrolysis with dilute aqueous alkali or even by exposure to moist air or heating with water.[5] It is important to note that performic acid is preferably not prepared separately, because it is unstable and loses oxygen rapidly,[46, 47, 53, 54] but it is prepared and utilized *in situ*.[4] Somewhat more complete hydroxylation is obtained by employing 90% hydrogen peroxide instead of the 25–30% concentration.[48]

Concentrated solutions of performic acid can be used in the hydroxylation of α,β-unsaturated acids to give fair yields of dihydroxy acids within a relatively short time.[55] Dilute solutions of organic peracids either are ineffective in hydroxylation of such compounds, or extremely long reaction times are required during which loss of active oxygen occurs.

The performic acid oxidation of ethylenic compounds having a hydroxyl group on a carbon atom directly adjacent to the ethylenic group yields appreciable amounts of acidic chain cleavage products in addition to about 50% of the expected hydroxylation products.[56]

In the peracetic and performic acid hydroxylation of compounds containing both an ethylenic and an acetylenic linkage only the double bond is attacked.[34a, 57-60]

Ethylenic compounds converted to α-glycols by oxidation with performic acid are listed in Table I.

Perbenzoic, Monoperphthalic, or Percamphoric Acid. These acids can be employed for the preparation of α-glycols from olefins by hydrolyzing the oxiranes which are formed first. In general, there is no advantage in employing the aromatic peracids to prepare α-glycols when two more-efficient peracids (performic and peracetic acid) are available for this purpose. In the presence of water or with unusually long reaction times, reactions have been reported in which α-glycols or their monobenzoates rather than oxiranes were obtained from oxidations of olefins with perbenzoic acid.

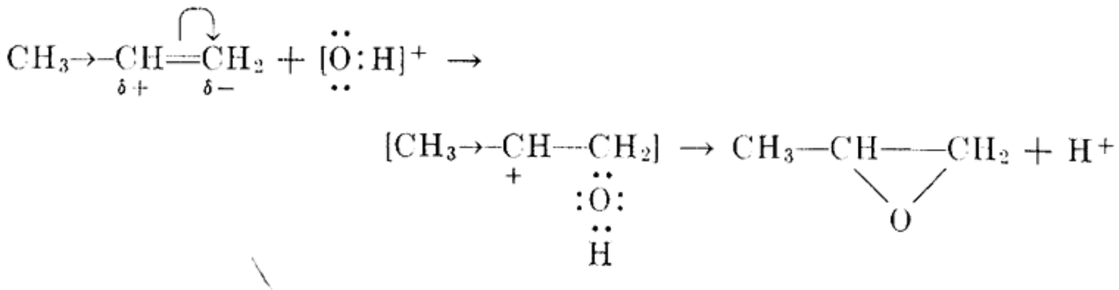
Ethylenic compounds which have been converted to α-glycols or to hydroxybenzoates by oxidation with perbenzoic acid are listed in Table I.

STEREOCHEMISTRY AND MECHANISM

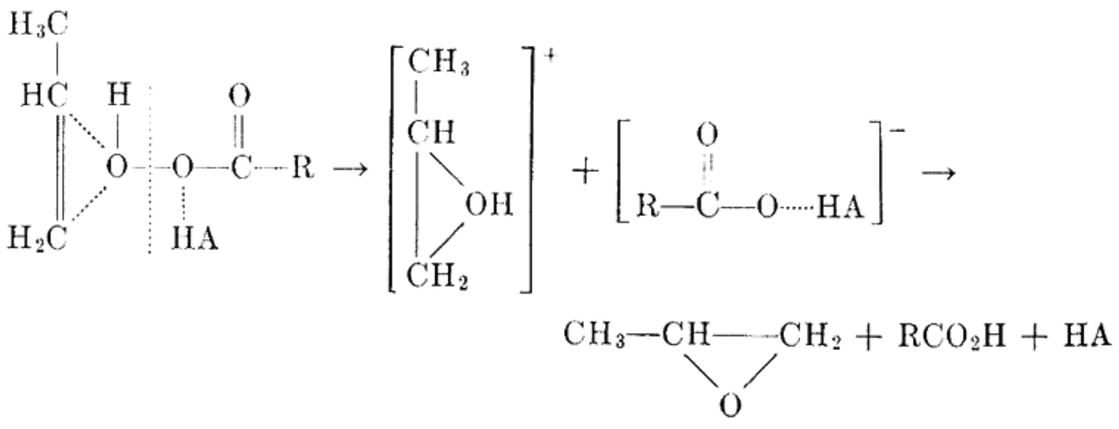
Although the structure of organic peracids, usually written RCO_3H, is not known, it is evident from their numerous and varied reactions that they are electrophilic reagents.[19] As the nucleophilic nature of an olefin is increased by replacement of the hydrogen atoms of its ethylenic linkage with electron-releasing groups, the rate of reaction with organic peracids increases considerably (see p. 388). Since peracid reactions investigated so far are subject to general acid catalysis,[61, 62] it has been

[49] Hilditch, *J. Chem. Soc.*, **1926**, 1828.
[50] Hilditch and Lea, *J. Chem. Soc.*, **1927**, 3106.
[51] Scanlan and Swern, *J. Am. Chem. Soc.*, **62**, 2305 (1940).
[52] Scanlan and Swern, *J. Am. Chem. Soc.*, **62**, 2309 (1940).
[53] Toennies and Homiller, *J. Am. Chem. Soc.*, **64**, 3054 (1942).
[54] Swern and Findley, unpublished results.
[55] English and Gregory, *J. Am. Chem. Soc.*, **69**, 2120 (1947).
[56] Ross, Gebhart, and Gerecht, *J. Am. Chem. Soc.*, **71**, 282 (1949).
[57] Evans, Fraser, and Owen, *J. Chem. Soc.*, **1949**, 248.
[58] Malenok, *J. Gen. Chem. (U.S.S.R.)*, **9**, 1947 (1939) [*C. A.*, **34**, 4385 (1940)].
[59] Malenok and Sologub, *J. Gen. Chem. (U.S.S.R.)*, **6**, 1904 (1936) [*C. A.*, **31**, 4285 (1937)].
[60] Raphael, *J. Chem. Soc.*, **1949**, S44.
[61] Friess, *J. Am. Chem. Soc.*, **71**, 2571 (1949).
[62] Waters, *J. Chem. Soc.*, **1948**, 1574.

proposed that the attacking moiety in peracid oxidations is the electropositively polarized (electrophilic) hydroxyl group $[\ddot{O}:H]^+$.[63, 64] The reaction of an olefin, such as propylene, with a peracid may, therefore, be represented as follows.[10]



This simple formulation, however, does not account for the striking stereospecificity of the reaction which precludes a free carbonium ion intermediate. A more reasonable alternative mechanism would involve essentially direct formation of the conjugate acid of the oxirane by donation of $[\ddot{O}:H]^+$ to the olefin by a peracid-general acid complex in a manner similar to that shown in the accompanying equation. The olefin-



$[\ddot{O}:H]^+$ part of the transition state of such a process would be similar to the so-called π-complexes.[65] This mechanism obviates any necessity for postulation of rapid and reversible $[\ddot{O}:H]^+$ formation from peracid and general acid (HA) followed by a slow attack of $[\ddot{O}:H]^+$ on the double bond. It is also a more reasonable reaction path in the non-polar solvents often used as reaction media.

As discussed earlier (pp. 380–385) the product isolated may be the

[63] Weisenborn and Taub, *J. Am. Chem. Soc.*, **74**, 1329 (1952).
[64] Roitt and Waters, *J. Chem. Soc.*, **1949**, 3060.
[65] M. J. S. Dewar, *The Electronic Theory of Organic Chemistry*, Oxford University Press, 1949.

oxirane or the hydroxy acyloxy compound, depending on the experimental conditions, the peracid used, and the stability of the oxirane.

The initial oxidation step in epoxidation and hydroxylation with organic peracids is the same, and it has generally been assumed that this reaction proceeds by *cis* addition to the double bond.[5, 66] Recently, unequivocal evidence was obtained to substantiate this assumption. It was shown by x-ray diffraction and infrared absorption studies that oleic acid and oleyl alcohol (both *cis* olefins) yield *cis*-9,10-epoxystearic acid and *cis*-9,10-epoxyoctadecanol, respectively, on epoxidation with peracetic or perbenzoic acid, and the corresponding *trans* olefins, elaidic acid and elaidyl alcohol, yield *trans*-9,10-epoxystearic acid and *trans*-9,10-epoxyoctadecanol, respectively.[67]

Opening of the oxirane ring, in the preparation of α-glycols from the corresponding oxiranes, is accompanied by inversion whether the reaction is conducted in neutral, acidic, or alkaline media.[5] The only exception to this generalization apparently is the opening of an oxirane ring in the terminal position of an aliphatic chain. In this case, if the ring-opening reagent attacks the terminal position, inversion cannot occur.[68, 69] A reaction scheme correlating the configurational relationships in the conversion of oleic and elaidic acids (*cis*- and *trans*-9-octadecenoic acids, respectively) to 9,10-dihydroxystearic acids by way of the intermediate oxiranes has recently been published.[5] This scheme is self-consistent and is in harmony with accepted theories of inversions, double-bond addition reactions, and the vast amount of experimental data available. This reaction sequence is undoubtedly of general applicability to other olefins with non-terminal double bonds.

It should be noted that the oxirane obtained by epoxidation of an olefin with organic peracids (*cis* addition) is identical with that obtained by hypohalogenation (*trans* addition) followed by dehydrohalogenation (inversion occurs). In the latter preparative procedure two inversions have occurred; this gives the same stereochemical result as no inversions.

Hydroxylation of olefins with potassium permanganate,[70–73] *t*-butyl hydroperoxide (osmium tetroxide catalyst),[74, 75, 76] or by photochemical

[66] Braun, *J. Am. Chem. Soc.*, **51**, 228 (1929).
[67] Witnauer and Swern, *J. Am. Chem. Soc.*, **72**, 3364 (1950).
[68] Abderhalden and Eichwald, *Ber.*, **48**, 1847 (1915).
[69] Sowden and Fischer, *J. Am. Chem. Soc.*, **64**, 1291 (1942).
[70] Böeseken, *Rec. trav. chim.*, **47**, 683 (1928).
[71] Böeseken and Cohen, *Rec. trav. chim.*, **47**, 839 (1928).
[72] King, *J. Chem. Soc.*, **1943**, 37.
[73] Kuhn and Ebel, *Ber.*, **58**, 919 (1925).
[74] Milas, *J. Am. Chem. Soc.*, **59**, 2342 (1937).
[75] Milas and Sussman, *J. Am. Chem. Soc.*, **58**, 1302 (1936).
[76] Milas, Sussman, and Mason, *J. Am. Chem. Soc.*, **61**, 1844 (1939).

addition of hydrogen peroxide to the double bond [77] proceeds by *cis* addition. Catalytic hydroxylation of olefins with hydrogen peroxide and other inorganic catalysts, such as pertungstic acid, pervanadic acid, or selenium dioxide, however, proceeds by *trans* addition.[78]

SELECTION OF EXPERIMENTAL CONDITIONS

Since the oxirane group is extremely reactive and undergoes ring opening with various types of compounds which contain active hydrogen atoms, it is obvious that conditions for epoxidation must be selected with care. It is of paramount importance to avoid high reaction temperatures [1] and to exclude strongly acidic materials from the reaction mixtures [4] if high yields are to be obtained. In epoxidations with perbenzoic and monoperphthalic acids an inert solvent is employed; in epoxidations with peracetic acid, acetic acid may be used as the solvent, provided that strong acids are absent and reaction temperatures below about 30° are employed.

With unsaturated substances containing isolated double bonds, such as 2-pentene, 2-butene, oleic acid, and oleyl alcohol, epoxidation is rapid and is usually complete within eight to twenty-four hours at room temperature or below. If electron-releasing groups are attached to or are in close proximity to the ethylenic linkage, as in 2-methylpropene, 2-methyl-2-butene, and tetramethylethylene, the reaction is considerably accelerated; [10] if electron-attracting groups are attached to or are in close proximity to the ethylenic linkage, as in cinnamic, maleic, fumaric, crotonic, 2-pentenoic, and 2-hexenoic acids and their esters, the reaction is slowed down.[10] The wide range of specific reaction rates in related groups of compounds is shown most strikingly by comparing ethylene ($k \times 10^3 = 0.19$) with 2-methyl-2-butene ($k \times 10^3$ = ca. 1000), cyclobutene ($k \times 10^3 = 21$) with 1-methylcyclopentene ($k \times 10^3 = 2200$), sorbic acid ($k \times 10^3 = 0.04$) with oleic acid ($k \times 10^3 = 384$), allylbenzene ($k \times 10^3 = 2.0$) with 1-phenyl-1-propene ($k \times 10^3 = 46$), 1,4-dihydronaphthalene ($k \times 10^3 = 37$) with 1,2-dihydronaphthalene ($k \times 10^3 = 230$–240), cinnamic acid ($k \times 10^3 = 0.13$) with cinnamyl alcohol ($k \times 10^3 = 203$), 1-phenyl-2-butene ($k \times 10^3 = 10$) with 1-phenyl-1-butene ($k \times 10^3 = 80$), eugenol ($k \times 10^3 = 2.2$) with isoeugenol ($k \times 10^3 = 127$), and safrole ($k \times 10^3 = 1.3$) with isosafrole ($k \times 10^3 = 148$).[10,79] Furthermore, the specific reaction rate of tetramethylethylene with peracetic acid at 25.8° is too high to be measured.[80,81] Selected references describing kinetic studies are 2, 28, and 80–88.

[77] Milas, Kurz, and Anslow, *J. Am. Chem. Soc.*, **59**, 543 (1937).
[78] Mugdan and Young, *J. Chem. Soc.*, **1949**, 2988.
[79] Swern, *Chem. Revs.*, **45**, 1 (1949).

The rates of oxidations with peracids can be determined readily with a minimum of experimental effort by measuring unconsumed peroxide at suitable time intervals.[11,13,89,90,91] By following the disappearance of active oxygen, the reaction can be terminated at exactly the right time, thereby minimizing side reactions and loss of active oxygen. Furthermore, the determination of unconsumed peroxide should be carried out in all peracid oxidations in which distillation techniques are employed in the recovery of solvent and in the isolation of reaction products. *In reactions which proceed slowly, a large amount of unconsumed peracid may be present in the distillation charge and cause an explosion if the peroxide is not destroyed.*

Although a wide range of conditions can be employed in the preparation of α-glycols, temperatures above 50° are undesirable because significant loss of active oxygen occurs. Early workers, who were not concerned with efficient use of active oxygen, operated at high temperatures and of necessity employed large excesses of hydrogen peroxide or peracid. Reaction temperatures below 5–10° may also be disadvantageous since they make the reaction time objectionably long.

To help in the selection of hydroxylation techniques, the methods just discussed are listed in decreasing order of efficiency and over-all desirability from the laboratory standpoint.

1. Oxidation with 30% hydrogen peroxide in formic acid solution at 40°; 1.025–1.05 moles of hydrogen peroxide per ethylenic linkage.[2,4] This method is admirably suited for the hydroxylation of isolated double bonds and is probably the best hydroxylation technique employing organic peracids. See also method 3.

2. Oxidation with 30% hydrogen peroxide in acetic acid solution containing catalytic quantities of sulfuric acid at 40°; 1.025–1.05 moles of hydrogen peroxide per ethylenic linkage.[2,4]

[80] Böeseken and Stuurman, *Proc. Acad. Sci. Amsterdam*, **39**, 2 (1936) [*C. A.*, **30**, 3304 (1936)].
[81] Böeseken and Stuurman, *Rec. trav. chim.*, **56**, 1034 (1937).
[82] Bodendorf, *Arch. Pharm.*, **268**, 491 (1930).
[83] Böeseken and Blumberger, *Rec. trav. chim.*, **44**, 90 (1925).
[84] Böeseken and Hanegraaff, *Rec. trav. chim.*, **61**, 69 (1942).
[85] Heinänen, *Ann. Acad. Sci. Fennicae*, **A59**, No. 13, 3 (1943) [*C. A.*, **41**, 2307 (1947)].
[86] Smit, *Rec. trav. chim.*, **49**, 686 (1930).
[87] Stuurman, *Proc. Acad. Sci. Amsterdam*, **38**, 450 (1935) [*C. A.*, **29**, 4657 (1935)].
[88] J. Stuurman, thesis, University of Delft, 1936.
[89] Kolthoff and Menzel, *Die Massanalyse*, Vol. II, 2nd ed., p. 413, Springer, Berlin, 1931.
[90] Marks and Morrell, *Analyst*, **54**, 503 (1929).
[91] Wheeler, *Oil and Soap*, **9**, 89 (1932).

3. The same as 1 and 2, but employing 90% hydrogen peroxide.[48, 55] Although slightly more complete reaction is obtained with 90% hydrogen peroxide, the hazards attendant upon its use make it less desirable for laboratory investigation.[92, 93, 94] By use of the more concentrated peracids, however, ethylenic linkages adjacent to carboxyl groups can be hydroxylated readily.[55]

4. Prior preparation of performic or peracetic acids and employment of the peracids under conditions similar to 1, 2, and 3 above.

5. Epoxidation with peracetic, perbenzoic, or monoperphthalic acid, followed by hydrolysis. The only virtue of this technique, probably, is that one can obtain either the oxirane or the α-glycol from a given unsaturated substance.

Because of the instability of performic acid, there is usually little point in its separate preparation (method 4). If it is prepared separately, however, it should be used immediately. Performic acid of 90% strength is highly explosive.[94a] In contrast to performic acid, peracetic acid is relatively stable and can be stored conveniently. In the absence of catalysts, concentrated solutions of peracetic acid are fairly stable at room temperature (15–25°); 87–95% solutions remain virtually unchanged on standing for about five weeks,[46] the 50% solution shows no loss of peracid after storage for two weeks,[46] and the 45% solution retains 75% of the peracid after seven weeks.[47] The 45% solution retains 94% of the peracid after seven weeks of storage if it is stabilized with sodium pyrophosphate [47] (other stabilizers have also been suggested).[95, 96] Five to ten per cent solutions of peracetic acid in acetic acid, however, show significant losses of active oxygen at room temperature but little loss at 0 to 5°.[1] Although peracetic acid can be prepared by efficient processes and only a small amount of active oxygen is lost or unavailable for oxidative purposes, the separate preparation of the peracid is a time-consuming step in the hydroxylation reaction, and method 2 is more desirable. Concentrated solutions of peracetic acid have recently become commercially available.[97]

There is a wide variety of methods for preparing organic peracids, and many solvents have been suggested for use in their preparation, isolation, and application as oxidizing agents. This phase of peracid chemistry is

[92] Bellinger, Friedman, Bauer, Eastes, and Bull, *Ind. Eng. Chem.*, **38,** 310 (1946).

[93] Bellinger, Friedman, Bauer, Eastes, and Edmonds, *Ind. Eng. Chem.*, **38,** 627 (1946).

[94] Shanley and Greenspan, *Ind. Eng. Chem.*, **39,** 1536 (1947).

[94a] Weingartshofer-Olmos and Giguère, *Chem. Eng. News*, **30,** 3041 (1952).

[95] Naamlooze Venootschap Industrieele Maatschappij Voorheen Noury and Van Der Lande and Van Der Lande, Brit. pat. 234,163 [*C. A.*, **20,** 768 (1926)].

[96] Reichert, McNeight, and Elston, U. S. pat. 2,347,434 [*C. A.*, **39,** 89 (1945)].

[97] Buffalo Electrochemical Co., *Peracetic Acid Data Sheet* 1 (1947).

not sufficiently pertinent to be discussed here in detail, but information has recently been published on this subject.[79] The particular oxidative method and solvent selected will depend, in large part, on the solubility of the peracid and on the structure of the unsaturated substance and the oxidation products. Furthermore, the stability of the peracid and the oxidation products in the solvent medium and the ease of separation of the desired products from the other materials present have an important bearing on the selection of reaction conditions. The solvent has been reported to affect the rates of decomposition of peracids as well as their rates of reaction with unsaturated substances.[7, 13, 83, 98–101]

For information regarding other organic peracids (properties, methods of preparation, special techniques, etc.) reference 79 can be consulted.

EXPERIMENTAL PROCEDURES

Caution. *All preparations of and reactions with organic peracids should be conducted behind a safety shield, because a reaction occasionally proceeds with uncontrollable violence.* When an olefin of unknown structure or one that contains at least three electron-releasing groups attached to or in close proximity to the ethylenic linkage is epoxidized or hydroxylated for the first time, the reaction should be run on a small scale (preferably 0.1 mole or less), and provision should be made for efficient cooling. Detailed information regarding the properties of concentrated hydrogen peroxide [92, 93, 94, 102–105] and organic peracids [79] has recently been published.

Peracid oxidation mixtures should not be distilled unless an analysis has indicated the absence or low concentration of active oxygen. When the peracid content is low, acetic and formic acids can be safely and completely distilled from oxidation reactions at or below room temperature by the use of low pressure. Peracids and other peroxides can be conveniently destroyed by the addition of ferrous sulfate, sodium bisulfite, or other reducing agents.

[98] Berezovskaya and Semikhatova, *Bull. acad. sci. U.R.S.S., Classe sci. math. nat.*, **1934,** 1583, 1589 [*C. A.*, **29,** 6130 (1935)].

[99] Calderwood and Lane, *J. Phys. Chem.*, **45,** 108 (1941).

[100] Lagrave, *Ann. Chim.*, [10] **8,** 363 (1927).

[101] Meerwein, Ogait, Prang, and Serini, *J. prakt. Chem.*, **113,** 9 (1926).

[102] Bretschger and Shanley, *Trans. Electrochem. Soc.*, **92,** 10 pp. (1947) preprint.

[103] McKee, *Mech. Eng.*, **68,** 1045 (1946).

[104] Médard, *Compt. rend.*, **222,** 1491 (1946).

[105] Schumb, *Ind. Eng. Chem.*, **41,** 992 (1949).

Analysis of Peracids

Perbenzoic Acid. Perbenzoic acid in an organic solvent can be determined iodimetrically by shaking the solution with an aqueous acetic acid solution of potassium iodide. A known volume of the perbenzoic acid solution is pipetted into an iodine flask containing 50 ml. of 0.4 *N* acetic acid and 1 g. of potassium iodide, the mixture is shaken, and the liberated iodine is titrated with 0.05–0.1 *N* sodium thiosulfate solution, starch indicator being used.

In following the course of the oxidation of water-insoluble substances which precipitate upon addition of the solution to the aqueous acetic acid, a sharper end point is obtained by adding the perbenzoic acid solution to 25 ml. of a chloroform-acetic acid solution (3:2 by volume). Two milliliters of saturated potassium iodide solution is added, and the mixture is allowed to stand for five minutes. Seventy-five milliliters of water is added, the solution is shaken, and the liberated iodine is titrated with 0.05–0.1 *N* sodium thiosulfate.[91] One milliliter of 0.1 *N* sodium thiosulfate is equivalent to 0.00690 g. of perbenzoic acid.

Monoperphthalic Acid. Monoperphthalic acid can be determined by the same methods employed for perbenzoic acid. An alternative procedure [106] is to add 2 ml. of the solution to 30 ml. of 20% aqueous potassium iodide and titrate the liberated iodine after 10 minutes with 0.05 *N* sodium thiosulfate solution. One milliliter of 0.05 *N* sodium thiosulfate is equivalent to 0.00455 g. of monoperphthalic acid.

Peracetic Acid. The peroxide components in the peracetic acid solutions described below are determined on a single sample as follows:[44,45] 0.2–2 ml. of the solution (accurately dispensed from a pipette or weighed) is diluted with 50 ml. of 4 *N* aqueous sulfuric acid which has been cooled to 0°. This solution is titrated rapidly with 0.1 *N* potassium permanganate to a pink end point. This determines unreacted hydrogen peroxide; 1 ml. of 0.1 *N* potassium permanganate is equivalent to 0.00170 g. of hydrogen peroxide. The peracetic acid is determined by adding 2 ml. of saturated aqueous potassium iodide to the same solution and rapidly titrating with 0.1 *N* sodium thiosulfate, starch indicator being used; 1 ml. of 0.1 *N* sodium thiosulfate is equivalent to 0.00380 g. of peracetic acid. At this point, the flask and its contents are heated on the steam bath for five to ten minutes, causing a return of the blue color, and liberated iodine is titrated with 0.1 *N* sodium thiosulfate. The last titration gives the diacetyl peroxide content; 1 ml. of 0.1 *N* sodium thiosulfate is equivalent to 0.00590 g. of diacetyl peroxide. It has been reported that ceric sulfate is more satisfactory than potassium permanganate for determination of residual hydrogen peroxide.[107]

[106] Böhme, *Org. Syntheses*, **20**, 70 (1940).

In following the consumption of active oxygen during the oxidation of water-insoluble substances with peracetic acid, the procedure described under the analysis of perbenzoic acid should be employed.[91] This determines total active oxygen and not peracetic acid alone, but the difference between the titrations at succeeding time intervals gives a measure of peracetic acid consumed.

Performic Acid. The procedures described in the analysis of peracetic acid are used.

Preparation of Peracids

Perbenzoic Acid (Benzoyl Peroxide-Sodium Methoxide Method). Directions published in *Organic Syntheses* [11] are probably the most satisfactory for preparing stable solutions of perbenzoic acid. Briefly, this method consists in (*a*) allowing benzoyl peroxide to react with sodium methoxide in chloroform-methanol solution, (*b*) extracting the sodium perbenzoate solution with water, (*c*) acidifying with sulfuric acid, and (*d*) extracting the perbenzoic acid with chloroform. Yields of perbenzoic acid of about 85% are obtained. *Do not recrystallize benzoyl peroxide from hot chloroform, as suggested in the original* Organic Syntheses *procedure, as this operation is hazardous.* Benzoyl peroxide may be purified safely by adding methanol to a chloroform solution of the peroxide at room temperature.[108] A recrystallized grade is commercially available.[109]

For preparation of large quantities of perbenzoic acid or solutions which are to be stored for a long time, a modified procedure has been recommended.[13]

(*a*) The mixture is kept below 0° during the addition of the chloroform solution of benzoyl peroxide to the methanol solution of sodium methoxide. Since this reaction is highly exothermic, a large quantity of salt-ice freezing mixture at −15° is employed to cool the reaction flask, the benzoyl peroxide solution is added at a slow, even rate of about 15–20 ml. per minute, and the reaction flask is swirled vigorously and continuously during the addition. There is no need to wait four to five minutes, as specified in the original procedure [11] before extracting the mixture with water.

(*b*) Instead of transferring the chloroform-methanol solution containing sodium perbenzoate to a separatory funnel, about 150 ml. of

[107] Greenspan and MacKellar, *Anal. Chem.*, **20**, 1061 (1948).
[108] Nozaki and Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).
[109] Lucidol Corporation, Buffalo, New York.

water containing chopped ice is added to the reaction mixture which is rapidly swirled. The mixture is then transferred to the separatory funnel, and 350 ml. of water containing chopped ice is added to the rapidly swirled material. In this way, the formation of lumps which dissolve slowly is prevented.

(*c*) The emulsion that collects at the interface of the aqueous sodium perbenzoate phase and the chloroform phase is discarded. Only three to five minutes is allowed for separation of the phases. Likewise, emulsions formed during the washing of the aqueous layer are discarded.

(*d*) The aqueous phase is washed with two 100-ml. portions of carbon tetrachloride, instead of chloroform.

(*e*) After acidification, the aqueous solution is extracted with reagent-grade benzene rather than chloroform. At this point, the temperature of the solution should be above 5°, to prevent freezing of the benzene.

(*f*) The benzene solution is washed with water, dried over anhydrous sodium sulfate (calcium chloride sometimes causes a sudden decomposition of the peracid [11]), and stored in the dark at about 10° until used.

Crystalline perbenzoic acid can be obtained by removal of the solvent under vacuum, as described in *Organic Syntheses*,[11] and purified by recrystallization from chloroform-ethanol mixtures [110] or from petroleum ether.[111] Perbenzoic acid melts at about 41° and is soluble in the common organic solvents, except cold petroleum ether.

Perbenzoic Acid (Benzaldehyde-Air Method).[3] The air oxidation of benzaldehyde in acetone solution irradiated with ultraviolet light is a convenient method for the preparation of moderately large quantities of perbenzoic acid.

In a 5-l. three-necked Pyrex flask equipped with a thermometer, a solid carbon dioxide-cooled reflux condenser, and two fritted glass disks reaching to the bottom of the flask, 520 g. (4.9 moles) of freshly distilled benzaldehyde is dissolved in 4 l. of acetone. The flask is immersed in an ice-water bath and irradiated from the top with three 125-watt Hanovia quartz mercury-vapor lamps, symmetrically placed around the flask, while a rapid stream of dry air is passed through the fritted disks and into the solution for twenty-four hours at 5–10°. The reaction is conducted in a fume hood because of the formation of ozone. If the reaction cannot be run without interruption, the acetone solution can be stored at 5–10° with little or no loss of perbenzoic acid. After about twenty-four hours, the rate of peracid formation decreases considerably

[110] Maan, *Rec. trav. chim.*, **48**, 332 (1929).

[111] Baeyer and Villiger, *Ber.*, **33**, 1569 (1900).

and the solution then contains about 2 moles of perbenzoic acid. The yield is 40–45%.

Monoperphthalic Acid. The procedure described in *Organic Syntheses*,[106] consisting in the reaction of phthalic anhydride with alkaline 30% aqueous hydrogen peroxide, is satisfactory, and gives 65–70% yields. It has been reported to be advantageous to employ 40% sodium hydroxide solution and to add crushed ice directly to the reaction mixture.[112] In this procedure, the peracid is extracted with ether, but, if ether is not a suitable solvent for the subsequent oxidation reactions, it can be removed readily and replaced by dioxane or other solvent by a procedure described in *Organic Syntheses*.[106]

Peracetic Acid.[1,47] In a 5-l. three-necked flask equipped with a mechanically driven glass stirrer, a thermometer, and a separatory funnel is placed 2250 g. of acetic anhydride, which has been filtered through glass wool to remove particles which may catalyze peroxide decomposition. The thermometer should be immersed in the liquid, and at least one neck of the flask should be open to the atmosphere. The acetic anhydride is warmed to 35–40° in a water bath into which cold or warm water can be run at will and removed rapidly if necessary. By means of the separatory funnel, 500 g. of 25–30% hydrogen peroxide is added in about one hour with agitation, the temperature being maintained at 40°. The reaction becomes mildly exothermic soon after the addition of hydrogen peroxide is started, and cooling is required for three to four hours after the addition is complete to maintain the temperature at 40° (bath temperature 25–30°). The solution is allowed to stand overnight at room temperature. The concentration of peracetic acid is then about 0.8–1.2 *M* (6–9%). The yield is 60–90%. The solution contains diacetyl peroxide and some unconverted hydrogen peroxide in addition to peracetic acid and acetic acid.

A concentrated solution of peracetic acid [47] is prepared by cautiously adding 9.1 g. of 90% hydrogen peroxide to a stirred solution of 10 g. of acetic acid and 0.11 ml. of concentrated sulfuric acid contained in a flask immersed in a water bath at 22–23°. At the end of four hours, the peracetic acid content of the solution is about 44%; it rises to a maximum of 46% within twelve to fifteen hours.

Performic Acid.[47,53,54] In a 500-ml. Erlenmeyer flask, 25 g. of 25–30% hydrogen peroxide and 250 g. of 98–100% formic acid are mixed at room temperature. Since the reaction is only mildly exothermic (temperature rise 1–2°), no cooling is required in batches of this size. The maximum content of performic acid (approximately 5%) is obtained within thirty

[112] Bachman and Cooper, *J. Org. Chem.*, **9**, 302 (1944).

to sixty minutes, as determined by the analytical techniques already described.

A concentrated solution of performic acid is prepared by cautiously adding 28.4 g. of 90% hydrogen peroxide to a stirred solution of 23.0 g. of 98–100% formic acid and 0.28 ml. of concentrated sulfuric acid contained in a flask immersed in a water bath at 22–23°.[47,55] Maximum performic acid concentration (approximately 35%) is reached within thirty minutes.

Performic acid solutions are unstable, and active oxygen is lost at a fairly rapid rate (several per cent per hour at room temperature); the solutions, therefore, should not be stored but should be used immediately.

Epoxidation with Perbenzoic Acid

1,2-Epoxyethylbenzene (Styrene Oxide).[12,113] To a solution of 42 g. (0.30 mole) of perbenzoic acid in 500 ml. of chloroform, prepared as described on p. 393, 30 g. (0.29 mole) of styrene is added. The solution is maintained at 0° for twenty-four hours, with frequent shaking during the first hour. At the end of twenty-four hours titration of an aliquot part of the solution shows that only the slight excess of perbenzoic acid remains. The benzoic acid is removed from the chloroform solution by shaking with several portions of 10% sodium hydroxide solution, the alkali is removed by washing with water, and the chloroform solution is dried over anhydrous sodium sulfate. Fractional distillation yields 24–26 g. (69–75%) of 1,2-epoxyethylbenzene, b.p. 101°/40 mm., as an almost colorless liquid.

***cis*-9,10-Epoxystearic Acid.**[3,30] To 750 ml. of an acetone solution of 0.4 mole of perbenzoic acid, prepared as described on p. 394, 85 g. (0.3 mole) of oleic acid [114,115,116] is added at 0–5°. The solution is allowed to stand for forty hours at room temperature and then cooled to −25° and filtered; the precipitate is washed once with cold acetone. The crude 9,10-epoxystearic acid (purity 95–99%) is a white powder weighing about 85 g. Two recrystallizations from acetone at 0 to −25° yields 55–60 g. of analytically pure *cis*-9,10-epoxystearic acid, m.p. 59.5–59.8°. Oxirane oxygen:[117] calcd., 5.36%; found, 5.33–5.37%. The yield is 62–67%.

[113] Hibbert and Burt, *Org. Syntheses*, **8**, 102 (1928); *Coll. Vol.* **I**, 494 (1941).
[114] Brown and Shinowara, *J. Am. Chem. Soc.*, **59**, 6 (1937).
[115] Swern, Knight, and Findley, *Oil and Soap*, **21**, 1 (1944).
[116] Wheeler and Riemenschneider, *Oil and Soap*, **16**, 207 (1939).
[117] Swern, Findley, Billen, and Scanlan, *Anal. Chem.*, **19**, 414 (1947).

1,2-Epoxy-2-methyl-3-butene (Isoprene Monoxide) (preferential oxidation of one ethylenic linkage in a conjugated diene).[118] To a stirred solution of 16 g. (0.235 mole) of isoprene in 50 ml. of ethyl chloride cooled in an ice bath a cold solution of 30 g. (0.217 mole) of perbenzoic acid in 150 ml. of ethyl chloride is added from a dropping funnel. The contents of the flask and dropping funnel are protected from moisture by drying tubes. After the perbenzoic acid solution has been added, the reaction flask is allowed to stand in a refrigerator until the oxidizing agent is completely consumed (approximately twenty-four hours). The solution is then shaken cautiously with double the calculated quantity of sodium bicarbonate solution (30 g. per 100 ml. of water) in a cooled separatory funnel until evolution of carbon dioxide ceases. The aqueous layer is discarded, and the ethyl chloride solution is dried overnight in a refrigerator with anhydrous sodium sulfate. The solution is filtered, and the filtrate is distilled through a Widmer column until unreacted isoprene begins to distill. The residual material is then fractionated twice and yields 7 g. (30–40%) of 1,2-epoxy-2-methyl-3-butene (isoprene monoxide).

Epoxidation with Monoperphthalic Acid

β- and α-Cholesteryl Oxide Acetates.[25] A solution of 10 g. (0.023 mole) of cholesteryl acetate, m.p. 112–114°, in 50 ml. of ether is mixed with 266 ml. of an ether solution containing 8.4 g. (0.046 mole) of monoperphthalic acid. The solution is refluxed for six hours, and the solvent is removed by distillation. The residue is dried under reduced pressure and digested with 250 ml. of chloroform which has been dried over anhydrous potassium carbonate. The mixture is filtered, yielding 6.7 g. of phthalic acid (87% recovery) and a colorless solution, from which the solvent is removed under reduced pressure. The residue is crystallized from 30 ml. of methanol, giving 6.0 g. (58% yield) of β-cholesteryl oxide acetate, which on recrystallization gives the pure product, m.p. 111–112°, $[\alpha]_D^{25} - 21.8°$. Concentration of the filtrate gives 1.55 g. (15% yield) of α-cholesteryl oxide acetate. The α-isomer, purified by crystallization from ethanol, has a m.p. of 101–103°, $[\alpha]_D^{25} - 44.6°$.

Hydroxylation with Hydrogen Peroxide-Acetic Acid

9,10-Dihydroxystearic Acid (High-Melting Isomer).[4] A well-stirred solution consisting of 270 g. (0.898 mole) of elaidic acid (containing 94% of elaidic acid and 6% of saturated acids), 810 ml. of glacial acetic

[118] Pummerer and Reindel, *Ber.*, **66**, 335 (1933).

acid, and 20 g. of concentrated sulfuric acid is heated to 40°, and 123 g. of 25.5% hydrogen peroxide (0.925 mole) is added dropwise over a period of fifteen minutes. The reaction is only slightly exothermic. A granular precipitate begins to form after about thirty minutes and increases in bulk as the oxidation proceeds. The total reaction time at 40° is five hours. The reaction mixture is then poured into several volumes of hot water (95–100°) and stirred well for several minutes. The mixture is cooled to room temperature and filtered, and the precipitate is washed well with cold water. The product, which weighs about 300 g. and consists of a mixture of 9,10-dihydroxystearic acid and hydroxyacetoxystearic acids, is heated at 100° for one hour with an excess of 2 *N* sodium hydroxide and then poured into excess hydrochloric acid, with stirring. The granular precipitate is filtered and washed free of acid. It weighs about 280 g. (93%) and consists of somewhat impure 9,10-dihydroxystearic acid, m.p. 125–128°. Crystallization from 95% ethanol (7 ml./g.) at 0–5° yields 220 g. (78%) of pure 9,10-dihydroxystearic acid as glistening plates, m.p. 130–131°.

Hydroxylation with Hydrogen Peroxide-Formic Acid

9,10-Dihydroxystearic Acid (Low-Melting Isomer).[4] To a well-stirred solution of 141 g. (0.5 mole) of oleic acid [114,115,116] in 423 ml. of 98–100% formic acid in a 1-l. three-necked flask at 25° is added during a fifteen-minute period 59 g. of 30% (100 volume) hydrogen peroxide solution (17.5 g.; 0.513 mole; 2.5% excess of hydrogen peroxide). The reaction becomes vigorously exothermic after five to ten minutes and the mixture becomes homogeneous in twenty to thirty minutes after all the hydrogen peroxide has been added. The temperature is kept at 40° with a cold-water bath at the start and a warm-water bath toward the end of the reaction. After about two hours no further consumption of peroxide is observed, and the formic acid is removed by distillation under reduced pressure (b.p. 50°/125 mm.) in a stream of carbon dioxide or nitrogen to prevent bumping. The residue in the flask, which consists of hydroxyformoxystearic acids, is heated for one hour at 100° with an excess of 3 *N* aqueous sodium hydroxide, and the hot, pale yellow solution is slowly poured into an excess of 3 *N* hydrochloric acid with stirring. The oil, which separates, is allowed to solidify, and the aqueous layer is discarded. The white solid is remelted with hot water on a steam bath and stirred well to remove residual salts and water-soluble acids. When the oil has resolidified, the aqueous layer is discarded, and the solid is broken into small pieces and air dried. This product consists of fairly pure 9,10-dihydroxystearic acid (iodine

number about 2–4, neutralization equivalent 315–320), weighs about 150–155 g. (97–99%), and melts at about 92°. The small quantity of unsaturated material present can be separated readily by grinding the material and washing it by decantation with several portions of petroleum naphtha (hexane fraction, boiling range 63–70°). 9,10-Dihydroxystearic acid, m.p. 93° and iodine number 0.0, is obtained from the crude product with a loss of about 6%. In order to obtain an analytically pure product, the dihydroxystearic acid is recrystallized from 95% ethanol, yielding 9,10-dihydroxystearic acid, m.p. 95°, in 80% overall yield.

If purified oleic acid is not available, red oil (commercial product containing about 60–75% oleic acid) may be employed. The crude 9,10-dihydroxystearic acid obtained from this material melts at about 70–75° (compared to 92° when pure oleic acid is used), and several recrystallizations from 95% ethanol are required to obtain a pure product. The yield of 9,10-dihydroxystearic acid from red oil is about 50–60% of the available oleic acid. Furthermore, the 90% grade of formic acid is satisfactory, but the reaction mixture remains heterogeneous throughout. In preparations one-tenth the size described, the 25–30% hydrogen peroxide can be added in one portion. In larger preparations the addition may require thirty minutes to one hour. In preparations five to ten times the size described, it is more convenient to pour the reaction mixture into a large volume of water and then hydrolyze the washed oily layer of hydroxyformates as described.

When 90% hydrogen peroxide is employed instead of the 30% grade, the crude dihydroxystearic acid has an iodine number of 1, instead of 2–4. With the concentrated peroxide, the quantity of formic acid can be reduced to about one-seventh the amount employed with 25–30% hydrogen peroxide.

1,2-Tetradecanediol.[2] To a well-stirred mixture of 49.2 g. (0.25 mole) of 1-tetradecene, b.p. 158–159°/60 mm., n_D^{20} 1.4357 (prepared by efficient fractional distillation of the 95% commercial grade), and 295 ml. of 98–100% formic acid at 25°, 35 g. of 25.6% hydrogen peroxide (0.263 mole; 5% excess) is added in one portion. The mixture is heated and stirred for about twenty-four hours at 40°, or until an analysis [91] indicates that the theoretical quantity of peroxide has disappeared. The reaction mixture is heterogeneous throughout. The formic acid is recovered under reduced pressure, and the distillation residue is refluxed for one hour with excess 3 *N* ethanolic potassium hydroxide. Most of the ethanol is then evaporated on the steam bath, and a large quantity of hot water is added, precipitating the glycol as an oil. When the glycol has solidified, the water layer is siphoned off, and the product is remelted

with hot water and allowed to resolidify. The combined water washes are extracted with ether to remove a small quantity of dissolved glycol, and the residue obtained after evaporation of the ether is combined with the main portion of glycol. The crude glycol is broken up into small pieces and air dried, yielding about 55 g. (95%) of fairly pure 1,2-tetradecanediol, m.p. about 65°; iodine number about 4. This is recrystallized from methanol (8 ml./g.) at 0°, yielding about 40 g. (69%) of pure product, m.p. 68–68.5°.

***trans*-1,2-Cyclohexanediol.**[55] To a mixture of 105 g. of 98–100% formic acid and 13 g. (0.115 mole) of 30% hydrogen peroxide, 8.0 g. (0.097 mole) of cyclohexene is added. The immiscible layers are shaken together briefly; spontaneous heating occurs, and the suspension becomes homogeneous at 65–70°, where it is held for two hours on the steam bath. Most of the formic acid is removed by distillation, and the residue is heated on the steam bath for forty-five minutes with 50 ml. of 20% sodium hydroxide. After cooling, the yellow solution is neutralized with hydrochloric acid and evaporated to dryness under vacuum. The resulting solid is distilled, yielding 10.25 g. of a fraction, b.p. 128–132°/15 mm., which solidifies immediately. Recrystallization from acetone gives 7.9 g. (70%) of *trans*-1,2-cyclohexanediol, m.p. 102–103°. A larger scale oxidation of cyclohexene is described in *Organic Syntheses*.[119]

Hydroxylation with Performic Acid

2,3-Dihydroxynonanoic Acid.[55] Twenty grams (0.13 mole) of 2-nonenoic acid is added slowly to a well-stirred solution of performic acid prepared by the reaction of 69 g. of 98–100% formic acid, 19 g. (0.5 mole) of 90% hydrogen peroxide, and 0.50 g. of concentrated sulfuric acid. The emulsified mixture is heated to 55–60° to start the reaction and is then held at this temperature for two hours while stirring is continued. The temperature is then allowed to rise to 95° until the spontaneous reaction is over (twenty-five minutes) and the excess peracid largely destroyed. Most of the formic acid is removed by vacuum distillation, and the residue is saponified on the steam bath for one-half hour with 175 ml. of 10% sodium hydroxide. After acidification with hydrochloric acid, the oily product is extracted with ether and the extract is dried over anhydrous sodium sulfate. Evaporation of the ether yields a waxy solid which is suspended in benzene and filtered, yielding 2,3-dihydroxynonanoic acid as white slippery flakes. Concentration of the filtrate followed by addition of ligroin gives two additional crops,

[119] Roebuck and Adkins, *Org. Syntheses*, **28,** 35 (1948).

the total yield of product being 12.4 g. (51%). On crystallization from ethyl acetate or water, pure 2,3-dihydroxynonanoic acid, m.p. 118–118.5°, is obtained.

TABLE OF ETHYLENIC COMPOUNDS OXIDIZED WITH ORGANIC PERACIDS

The following table lists the ethylenic compounds which have been epoxidized or hydroxylated with organic peracids. The table is divided into the following sections: A, Hydrocarbons and substituted hydrocarbons; B, Steroids (alphabetical order); C, Acids; D, Alcohols; E, Esters; F, Aldehydes and ketones (including carbohydrates); G, Ethers; H, Miscellaneous.

In the preparation of the table the literature has been consulted to October 1951. The addendum to Table I lists the compounds whose epoxidation or hydroxylation with organic peracids was reported from October 1, 1951, to October 1, 1952.

TABLE I

Ethylenic Compounds Oxidized with Organic Peracids

Ethylenic Compound		Yield of Oxirane, % (Reference)			Yield of α-Glycol, % (Reference)		
Formula	Name	Perbenzoic Acid	Monoperphthalic Acid	Peracetic Acid	Peracetic Acid	Performic Acid	Perbenzoic Acid
	A. Hydrocarbons and Substituted Hydrocarbons						
C_2H_4	Ethylene-C^{14}	30–53 (120)					
C_4H_6	1,3-Butadiene	42 (118, 121)				73 (122)	
$C_4H_6Br_2$	1,4-Dibromo-2-butene					Low (123)	
$C_4H_6Cl_2$	1,4-Dichloro-2-butene					30 (123)	
	3,4-Dichloro-1-butene					— (123)	
C_4H_7Cl	3-Chloro-2-methyl-1-propene (methallyl chloride)				70 (124)		
C_4H_8	1-Butene					— (122)	
	2-Butene				54 (71)	85 (122)	
C_5H_7Cl	1-Chloro-1-cyclopentene	75–80 (125, 126)					
	1-Chloro-2-cyclopentene	75–80 (125, 126)					
C_5H_8	Cyclopentene	80–90 (70, 127)					
	Isoprene	30–60 (118, 121, 128)			— (129)		
	3-Methyl-1,2-butadiene				— (129)		
	1,4-Pentadiene	— (121)					
C_5H_{10}	Amylenes			— (23)			
C_6H_7N	1-Cyano-2-cyclopentene	— (130)					
C_6H_8	1,3-Cyclohexadiene	85–90 (131)					
C_6H_9Cl	1-Chloro-1-cyclohexene	75–80 (125, 126, 132, 133)					
	1-Chloro-2-cyclohexene	75–80 (125, 126, 134)					
C_6H_{10}	Biallyl	— (135)					
	Cyclohexene	100 (70, 136)		60–67 (32, 137)	63–100 (32, 70, 138, 139, 140)	65–75 (55, 119, 122, 141)	30 (142)
	2,3-Dimethylbutadiene	— (121)					
	1,5-Hexadiene	66 (121, 143)					
	2,4-Hexadiene	— (121)					
	1-Methyl-1-cyclopentene	75 (10, 70, 144)					
	3-Methyl-1-cyclopentene	— (132)				58 (141, 144)	
	4-Methyl-1-cyclopentene	— (132)					
	5-Methyl-1-cyclopentene					65 (141)	
	5-Methylcyclopentenes (mixture of isomers)					70 (144)	
$C_6H_{11}BrO$	4-Methoxy-5-bromo-1-pentene	85 (145, 146)					
C_6H_{12}	2,3-Dimethyl-2-butene	— (7)					
	2-Methyl-2-pentene				— (147)		
$C_6H_{12}O$	2-Methyl-4-methoxy-1-butene	93 (148)					
C_7H_9N	3-Cyano-1-cyclohexene	— (130)					
$C_7H_{10}O$	2-Methyl-2,5-hexadien-4-one			— (149)			
$C_7H_{11}Cl$	2-Chloro-1-methyl-1-cyclohexene	— (126)					
	2-Chloro-4-methyl-1-cyclohexene	75–80 (125, 126, 134)					
	2-Chloro-1-methylenecyclohexane	— (150, 151)					
C_7H_{12}	Cycloheptene	100 (152)					
	2,3-Dimethyl-1-cyclopentene					59 (141)	
	3-Ethyl-1-cyclopentene					30 (141)	
	1,6-Heptadiene	— (121)					
	1-Methyl-1-cyclohexene	50–75 (10, 70, 136, 153)			— (140)	73 (141)	
	4-Methyl-1-cyclohexene	55 (132, 136, 154)				81 (141)	
	6-Methyl-1-cyclohexene	60–90 (136, 155)				40 (141)	
	3-Methyl-1-methylenecyclopentane	— (132)					
	Methylenecyclohexane	— (156)					
$C_7H_{12}O$	1-Ethoxy-1-cyclopentene	70 (125)					
$C_7H_{13}Cl$	1-Chloro-1-heptene	31 (157)					
C_7H_{14}	1-Heptene	— (158)			— (129)		
	5-Methyl-1-hexene	— (158)					
	3-Heptene	— (159)			— (129)		

TABLE I—*Continued*

ETHYLENIC COMPOUNDS OXIDIZED WITH ORGANIC PERACIDS

Ethylenic Compound		Yield of Oxirane, % (Reference)			Yield of α-Glycol, % (Reference)		
Formula	Name	Perbenzoic Acid	Monoperphthalic Acid	Peracetic Acid	Peracetic Acid	Performic Acid	Perbenzoic Acid
	A. Hydrocarbons and Substituted Hydrocarbons—Continued						
C_8H_8	Cycloöctatetraene	40–60 (160, 160*a*)		55 (161)			
	Styrene	69–75 (12, 22, 113, 162, 163, 164)				40 (122)	
$C_8H_8Br_2Cl_2$	7,8-Dichlorobicyclo-[4.2.0]-dibromo-octene	— (160)					
$C_8H_8Cl_2$	7,8-Dichlorobicyclo-[4.2.0]-2,4-octadiene	— (160)					
C_8H_{12}	1-Vinylcyclohexene	— (121)					
	4-Vinylcyclohexene				— (165)		
C_8H_{14}	Cycloöctene	65 (160)		69–80 (165*a*)			
	1,2-Dimethyl-1-cyclohexene	75 (166)					
	1,3-Dimethyl-1-cyclohexene	— (132)					
	2,4-Dimethyl-1-cyclohexene	— (132)					
	Dimethylcyclohexene	— (7)					
	2,5-Dimethyl-1,5-hexadiene	— (121)					
	3-Methyl-1-methylenecyclohexane	— (132)					
	1-*n*-Propyl-1-cyclopentene	— (132)					
	1-Isopropyl-1-cyclopentene	— (132)					
	1,7-Octadiene	— (121)					
$C_8H_{14}O$	1-Ethoxy-1-cyclohexene	70 (125)					
	3-Ethoxy-1-cyclohexene	— (155, 167)					
$C_8H_{15}Cl$	2-Chloro-2-octene	25 (157)					
C_8H_{16}	Diisobutylene	— (6, 7)			— (41, 43, 168)		
	2-Methyl-1-heptene				— (129)		
	1-Octene			35 (2)		58–70 (2, 169)	
	Octenes	15 (21)		28 (21)			
	2,4,4-Trimethyl-1-pentene	40 (36)		— (36, 40)	— (36, 40, 147)	— (36)	
	2,4,4-Trimethyl-2-pentene	70 (40)		— (36, 40)	— (36, 40, 147)	40 (40)	
$C_8H_{16}O_2$	1,1-Diethoxy-2-butene	25 (170)					
C_9H_8	Indene	100 (70, 132, 163, 171)			100 (138)		
C_9H_9Br	3-(*p*-Bromophenyl)-1-propene	— (172)					
	1-(*p*-Bromophenyl)-1-propene	80 (172)					
C_9H_9Cl	3-Chloro-1-phenyl-1-propene	— (170)					
C_9H_{10}	Allylbenzene	60–80 (173, 174)					
	1-Phenyl-1-propene	— (162, 175, 176)			100 (138)		
	2-Phenylpropene	80 (162, 177)					
C_9H_{14}	Hexahydroindene		— (178)				
C_9H_{16}	4-Methyl-2-ethylcyclohexene	— (132)					
	3-Methyl-1-ethylidenecyclohexane	— (132, 179, 180)					
	1,8-Nonadiene	— (121)					
	1-*n*-Propyl-1-cyclohexene	— (132)					
	1-Isopropyl-1-cyclohexene	— (132)					
C_9H_{18}	1-Nonene	100 (181)					
	Isononene						
$C_{10}H_{10}$	Dicyclopentadiene	70 (127, 171)			— (168)		
	1,2-Dihydronaphthalene	— (182)					
	2,3-Dihydronaphthalene	— (163)					
	1,4-Dihydronaphthalene	— (163, 182)					
	Divinylbenzene	— (121)			100 (139)		
	cis-1-Phenyl-1,3-butadiene	— (183)					
$C_{10}H_{11}Br$	1-(*p*-Bromophenyl)-1-butene	75 (172)					— (183)
	4-(*p*-Bromophenyl)-1-butene	75 (172)					
$C_{10}H_{11}Cl$	2-Chloro-1,2,3,4-tetrahydronaphthalene	75–80 (125)					
$C_{10}H_{12}$	1-Phenyl-2-methyl-1-propene	100 (184, 185, 186)					
	1-Phenyl-1-butene	— (175)					
	4-Phenyl-1-butene	60–80 (173, 174)					
	1,2,3,4-Tetrahydronaphthalene	— (136)					
$C_{10}H_{12}O$	1-Anisyl-1-propene	— (175)					
$C_{10}H_{14}$	5-Phenyl-1-pentene	60–80 (173, 174)					

TABLE I—*Continued*

ETHYLENIC COMPOUNDS OXIDIZED WITH ORGANIC PERACIDS

Ethylenic Compound		Yield of Oxirane, % (Reference)			Yield of α-Glycol, % (Reference)		
Formula	Name	Perbenzoic Acid	Monoperphthalic Acid	Peracetic Acid	Peracetic Acid	Performic Acid	Perbenzoic Acid
	A. Hydrocarbons and Substituted Hydrocarbons—Continued						
$C_{10}H_{16}$	Camphene	— (187)		— (188)			
	(+)-Δ^1-Carene				— (189)		
	(+)-Δ^3-Carene	70 (31)		69 (31, 188)	— (31)		
	2,4-Dimethyl-4-vinyl-1-cyclohexene	— (190)					
	Limonene	40–60 (6, 32, 101, 191, 192)		63 (32)	— (193)		
	Myrcene			25 (194)			
	Norbornylene				— (195)		
	Pinene	— (6, 187, 191, 196, 197)		89 (31, 198)			
	Sabinene						— (142)
	α-Terpinene	— (199)					
	γ-Terpinene	40 (200)					
$C_{10}H_{18}$	1-Butyl-1-cyclohexene	— (132)					
	1,9-Decadiene	— (121)					
	2,6-Dimethyl-2,6-octadiene	— (121)					
	3-Menthene	83–91 (201)		59–80 (201)	— (140)		
	4-Methyl-2-*n*-propyl-1-cyclohexene	— (132)					
$C_{10}H_{20}$	Caprylene	— (6, 191)					
	1-Decene	100 (181)		56 (2)		45–75 (2)	
	Decene	— (6)					
$C_{11}H_{10}$	1-Phenyl-3-penten-1-yne			50 (34)			
$C_{11}H_{10}O$	1-Anisyl-1-butene	— (175)					
$C_{11}H_{12}$	1-Phenyl-1-cyclopentene	— (10, 70, 202)					
	3-Phenyl-1-cyclopentene	90 (203*a*)					
$C_{11}H_{13}O_2$	1-(3,4-Methylenedioxyphenyl)-2-methyl-1-propene	60–80 (203, 204)					
$C_{11}H_{14}$	1-(*p*-Tolyl)-2-methyl-1-propene	60–80 (176, 203)					
	2-Methyl-3-phenyl-2-butene	— (205)					
	1-Phenyl-1-pentene	— (175)					
	1-Phenyl-2-methyl-1-butene	70–90 (184)					
	1-Phenyl-3-methyl-1-butene	— (175)					
$C_{11}H_{14}O$	1-Anisyl-2-methyl-1-propene	— (185, 186, 206)					
	1-(*m*-Methoxyphenyl)-2-methyl-1-propene	70–80 (207)					
	1-(*o*-Methoxyphenyl)-2-methyl-1-propene	70–80 (207)					
$C_{11}H_{18}$	2-Methylenedecahydronaphthalene	— (132)					
$C_{11}H_{22}$	1-Hendecene	100 (181)					
$C_{12}H_{12}$	1-Phenyl-3-hexen-1-yne			62 (34)			
$C_{12}H_{12}O_4$	3,4-Diacetoxystyrene	— (164)					
$C_{12}H_{14}$	1-Phenyl-1-cyclohexene	100 (10, 70, 208, 209)					
$C_{12}H_{14}O$	1-Anisyl-1-cyclopentene	— (202)					
	3-Anisyl-1-cyclopentene	— (203*a*)					
$C_{12}H_{16}$	1-Phenyl-2-ethyl-1-butene	70–90 (184)					
	1-Phenyl-2-methyl-1-pentene	70–90 (184)					
	6-Phenyl-1-hexene	60–80 (173, 174)					
$C_{12}H_{16}O$	1-Anisyl-2-methyl-1-butene	— (210)					
	1-Anisyl-1-pentene	— (175)					
	3-Anisyl-2-pentene	— (210)					
$C_{12}H_{20}$	1,2,5-Trimethyl-5-isopropenyl-1-cyclohexene	— (190)					
$C_{12}H_{24}$	1-Dodecene	100 (181, 211)		52 (2)		40–75 (2, 212)	
	Isododecene				— (213)		
$C_{12}H_{24}O$	3-Ethoxy-4-propyl-3-heptene	— (214)					
$C_{13}H_{14}$	1-Phenyl-3-methyl-3-hexen-1-yne				40 (58)		
$C_{13}H_{16}$	1-Phenyl-4-methyl-1-cyclohexene	— (208)					
$C_{13}H_{18}$	1-Benzyl-1-cyclohexene	— (132)					

TABLE I—*Continued*

Ethylenic Compounds Oxidized with Organic Peracids

Ethylenic Compound		Yield of Oxirane, % (Reference)			Yield of α-Glycol, % (Reference)		
Formula	Name	Perbenzoic Acid	Monoperphthalic Acid	Peracetic Acid	Peracetic Acid	Performic Acid	Perbenzoic Acid
	A. Hydrocarbons and Substituted Hydrocarbons—Continued						
$C_{13}H_{18}O$	1-Anisyl-2-ethyl-1-butene	— (206)					
$C_{13}H_{26}$	1-Tridecene	100 (181)					
$C_{14}H_{10}Cl_2$	*trans*-4,4′-Dichlorostilbene	50 (215)					
$C_{14}H_{12}$	Allostilbene				— (216)		
	Isostilbene	— (217)		— (137)			
	Stilbene	60–100 (22, 185, 216, 217)		83–100 (137, 201)	— (216)		
	1,1-Diphenylethylene						13 (218)
$C_{14}H_{18}$	1-Phenyl-2-cyclohexylethylene		— (219)				
$C_{14}H_{18}O_2$	1-(2,3-Dimethoxyphenyl)-1-cyclohexene					70–80 (220)	
$C_{14}H_{20}O$	4-Anisyl-3-heptene	— (210)					
$C_{14}H_{24}$	1,1-Dicyclohexylethylene	76 (221)					
$C_{14}H_{28}$	1-Tetradecene			42 (2, 222)		69–95 (2, 223)	
$C_{15}H_{12}O_2$	1-Phenyl-2-(3,4-methylenedioxyphenyl)ethylene	— (203, 204)					
$C_{15}H_{14}$	1,1-Diphenyl-1-propene	— (100, 224, 225)					
	1,2-Diphenyl-1-propene	— (226)					
	1,3-Diphenyl-1-propene	— (175)					
	Diphenylpropene				100 (138)		
	1-Phenyl-2-(*p*-tolyl)ethylene	— (176, 203, 227)					
$C_{15}H_{14}O$	1-Phenyl-2-anisylethylene	— (185, 228)					
	1-Phenyl-1-(*m*-methoxyphenyl)ethylene	— (229)					
	1-Phenyl-1-(*o*-methoxyphenyl)ethylene	— (229)					
$C_{15}H_{18}$	1-Phenyl-3-nonen-1-yne			30 (33)			
$C_{15}H_{22}O$	1-Anisyl-2-propyl-1-pentene	— (206)					
$C_{15}H_{24}$	Hydrocarbon (Two C=C)	— (190)					
	Caryophyllene	70–100 (230, 231)					— (142)
	Copaene	100 (232)					
	(+)-Sesquiterpene	— (233)					
$C_{15}H_{26}$	Dihydrocaryophyllene	69 (230)		25 (234)			
$C_{16}H_{14}$	1,4-Diphenylbutadiene	— (121)					
$C_{16}H_{16}$	1,1-Diphenyl-2-methyl-1-propene	— (235)					
	2,3-Diphenyl-2-butene	— (235)					
	1,1-Diphenyl-1-butene	— (100, 224, 236)					
	1,1-Di-*p*-tolylethylene	— (237)					
	1,3-Diphenyl-2-methyl-1-propene	70–90 (184)					
$C_{16}H_{16}O_2$	1-Anisyl-1-(*m*-methoxyphenyl)ethylene	80 (229)					
	1-Anisyl-1-(*o*-methoxyphenyl)ethylene	— (229)					
$C_{16}H_{20}$	1-Phenyl-3-methyl-3-nonen-1-yne				Low (59)		
$C_{16}H_{32}$	1-Hexadecene			50 (2)	— (238, 239)	58–85 (2, 169)	
$C_{17}H_{18}$	1-Phenyl-2-benzyl-1-butene	70–90 (184)					
	1,1-Diphenyl-1-pentene	— (100)					
	1,1-Diphenyl-3-methyl-1-butene	— (100)					
$C_{17}H_{18}O$	1-Phenyl-1-anisyl-1-butene	— (225)					
$C_{17}H_{18}O_2$	1,1-Dianisyl-1-propene	— (225)					
$C_{18}H_{19}O_2$	1,1-Dianisyl-1-butene	— (225)					
$C_{18}H_{20}$	1,1-Diphenyl-1-hexene	85 (100)					
	1,1-Diphenyl-3-methyl-1-pentene	95 (100)					
	1-Phenyl-2-benzyl-1-pentene	70–90 (184)					
	1-Phenyl-2-benzyl-3-methyl-1-butene	70–90 (184)					
$C_{18}H_{36}$	1-Octadecene			<40 (2, 222)		50–75 (2, 169)	
	9-Octadecene	— (240)					
$C_{20}H_{16}$	Triphenylethylene	66–70 (100, 227, 241)					
$C_{21}H_{18}$	1,1,3-Triphenyl-1-propene	85 (100)					
$C_{21}H_{18}O$	1-Anisyl-2,2-diphenylethylene	90 (100, 227)					
$C_{22}H_{20}$	1-(2-Biphenylyl)-1-phenyl-1-methyl-1-propene		99 (242)				
	1,3-Diphenyl-2-benzyl-1-propene	— (185, 228)					
$C_{23}H_{22}O$	1-Anisyl-2-benzyl-3-phenyl-1-propene	— (206)					

TABLE I—*Continued*

ETHYLENIC COMPOUNDS OXIDIZED WITH ORGANIC PERACIDS

Ethylenic Compound		Yield of Oxirane, % (Reference)			Yield of α-Glycol, % (Reference)		
Formula	Name	Perbenzoic Acid	Monoperphthalic Acid	Peracetic Acid	Peracetic Acid	Performic Acid	Perbenzoic Acid
	B. Steroids (alphabetical order)—Continued						
	3-*trans*-Dehydroandrosterone	— (293)			— (293)		
	trans-Dehydroandrosterone acetate	50 (294)	25–60 (294, 295)				
	trans-Dehydroandrosterone benzoate		80 (294)				
	3-*trans*-Dehydroandrosterone tetraacetylglucoside				— (293)		
	Dehydroergosteryl acetate-maleic anhydride adduct	— (288)					
	Dehydroisoandrosterone	Fair (296)					
	Dehydroisoandrosterone acetate	40 (297)			25–30 (298)		
	3,6-Diacetoxy-5-methyl-10-norandrost-8(9)-en-17-one		40 (299)				
	3,6-Diacetoxy-5-methylnorcholestane	20 (300)		30 (300)			
	3β,21-Diacetoxy-20-oxo-5-allo-14,16-pregnadiene	25 (301)	70 (259, 301)				
	Dibromodehydroergosteryl acetate-maleic anhydride adduct	80 (302)					
	3,7-Dihydroxycholenic acid	70 (303)					
	Dihydroergosteryl acetate						— (304)
	3α,12α-Dihydroxy-14-cholenic acid	— (305)					
	3,9-Epoxy-11-cholenic acid	60 (306)					
	α-Ergostenyl acetate						— (304)
	Ergosterol						20 (304)
	Ergosterol-maleic anhydride adduct			— (288)			
	Ergosteryl acetate-maleic anhydride adduct	— (302)					
	9-Etiocholenol-3α-one-17	— (308)					
	11-Etiocholen-3α-ol-17-one acetate	>60 (309)					
	3α-Hydroxy-9,11-cholenic acid	25 (306)					
	3α-Hydroxy-11-cholenic acid	80 (310)					
	3α-Hydroxypregnan-20-one enol acetate	— (258)					
	Δ^2-22-Isoallospirostene	71 (315)					
	$\Delta^{9(11)}$-22-Isoallospirosten-3β-ol-3-acetate	56 (311)					
	Isodihydroxycholenic acid	— (312)					
	3-Ketoandrosta-4,16-diene	70 (313)					
	6-Methoxy-16-*i*-pregnen-20-one	— (314)					
	Methyl 3β-acetoxy-14,16-alloetiocholadienate	— (316)					
	Methyl 3β-acetoxyallo-14-etiocholenate		80 (269)				
	Methyl 3β-acetoxy-5,14,16-cholatrienate		— (317)				
	Methyl 3α-acetoxy-9,11-cholenate	60–70 (264, 288, 318)					
	Methyl 3α-acetoxy-11-cholenate	50 (318, 319)					
	Methyl 3β-acetoxy-11-cholenate	40 (319)					
	Methyl 3β-acetoxy-14,16-etioallocholadienate	— (259, 307)					
	Methyl 3β-acetoxy-14,16-etiocholadienate		100 (320)				
	Methyl 3α-acetoxy-9(11)-etiocholanate	— (321)					
	Methyl 3β-acetoxy-3β-etioallocholenate	— (259)					
	Methyl 3α-acetoxy-12α-hydroxy-7-cholenate	30 (322)					
	Methyl 3β-acetoxy-14,17-isoalloetiocholenate		80 (269)				
	Methyl 9-cholenate	— (323)					
	Methyl 11-cholenate	— (318, 324)					
	Methyl 7,14-3α,12β-diacetoxycholadienate	— (274)					

TABLE I—*Continued*

Ethylenic Compounds Oxidized with Organic Peracids

Ethylenic Compound		Yield of Oxirane, % (Reference)			Yield of α-Glycol, % (Reference)		
Formula	Name	Perbenzoic Acid	Monoperphthalic Acid	Peracetic Acid	Peracetic Acid	Performic Acid	Perbenzoic Acid
	B. Steroids (alphabetical order)—Continued						
	Methyl 3α,12α-diacetoxy-14-cholenate	— (259)					
	Methyl 3α,12β-diacetoxy-14-cholenate	50 (274)					
	Methyl diacetylapocholate	— (312)					
	Methyl 3α,12β-diacetylapocholate	— (274)					
	Methyl 3,7-dihydroxycholenate	— (271)					— (272)
	Methyl 3α-hydroxy-11-cholenate	45 (319)					
	Methyl 3β-hydroxy-11-cholenate	55 (319)					
	Methyl 3α-hydroxy-12-methoxy-9,11-cholenate	95 (325)					
	Methyl 3-keto-4,11-choladienate	— (326)					
	Methyl 3-keto-11-cholenate	70 (326)					
	Methyl 9(11)-lithocholenate		>40 (327)				
	Methyl 12-methoxy-9,11-cholenate	— (325)					
	5-Methylnorcholestane-3,6-dione			55 (300)			
	3-Methyl-A-nor-3(5)-cholestene		— (328)				
	5,16-Pregnadien-3β-ol-20-one acetate	56 (314, 329)					
	14,17-Pregnadien-3-one		— (330)				
	5-Pregnen-20-one-3β-21-diol 21-monoacetate	70 (297)					
	Pregnenonol acetate				25 (298)		
	17-Vinyl-3,17-isoandrostanediol		65 (263, 331)				

	C. Acids						
$C_4H_6O_2$	Crotonic	20 (332)					63–4 (66)
	Isocrotonic						62–3 (66)
$C_5H_8O_2$	Allylacetic				— (333)		
	2-Pentenoic						75 (334)
$C_6H_8O_2$	Sorbic				— (103)		
$C_6H_8O_4$	Allylmalonic				— (103)		
$C_6H_{10}O_2$	2-Hexenoic						46 (334)
$C_9H_8O_2$	Cinnamic						— (55)
$C_9H_{16}O_2$	2-Nonenoic					25–51 (55)	
$C_{11}H_{18}O_2$	1,1,3-Trimethyl-3-cyclohexene-2-acetic		— (335)				
$C_{11}H_{20}O_2$	2-Hendecenoic					46 (55)	
	10-Hendenoic (undecylenic)	25–50 (336)			95 (333, 337, 338)	44–100 (4, 48, 169)	
$C_{15}H_{22}O_5$	ψ-Santonic	— (339)					
$C_{17}H_{31}BrO_2$	16-Bromo-9-hexadecene-1-carboxylic				— (340)		
$C_{18}H_{30}O_2$	9,11,13-Octadecatrienoic (eleostearic)				— (341)		
	9,12,15-Octadecatrienoic (linolenic)	— (342, 343)					
$C_{18}H_{32}Br_2O_2$	12,13-Dibromooctadecenoic				— (344)		
$C_{18}H_{32}O_2$	9,12-Octadecadienoic (linoleic)				Low (345, 346)		— (347)
$C_{18}H_{34}O_2$	*cis*-2-Octadecenoic				55 (348)		
	trans-2-Octadecenoic				7–37 (348)		
	trans-6-Octadecenoic (petroselaidic)					— (349)	
	cis-7-Octadecenoic					75–82 (349, 350)	
	trans-7-Octadecenoic			— (351)		73 (349, 350)	
	cis-8-Octadecenoic					61–73 (349, 350)	
	trans-8-Octadecenoic				89 (352)	80 (349, 350)	
	cis-9-Octadecenoic (oleic)	60–80 (3, 5, 22, 171, 240, 342, 343, 353, 354)		82 (1, 5, 20, 23, 355)	60–95 (4, 5, 29, 48, 49, 51, 72, 139, 352, 356–364)	60–100 (4, 5, 48, 169, 350, 365)	— (359)
	trans-9-Octadecenoic (elaidic)	Good (5, 171, 240, 366)		71 (1, 5, 72)	75–100 (4, 5, 29, 49, 72, 352, 357, 359, 363, 366)	80–100 (4, 5, 169, 349, 350)	— (359)

TABLE I—*Continued*

ETHYLENIC COMPOUNDS OXIDIZED WITH ORGANIC PERACIDS

Ethylenic Compound		Yield of Oxirane, % (Reference)			Yield of α-Glycol, % (Reference)		
Formula	Name	Perbenzoic Acid	Monoperphthalic Acid	Peracetic Acid	Peracetic Acid	Performic Acid	Perbenzoic Acid
			C. Acids—Continued				
$C_{18}H_{34}O_2$—(*Cont'd*)	*cis*-10-Octadecenoic					69 (350)	
	trans-10-Octadecenoic					88 (350)	
	cis-11-Octadecenoic		— (366*a*)			73–94 (350, 366*a*, 367)	
	trans-11-Octadecenoic					80–94 (349, 350, 367*a*)	
	cis-12-Octadecenoic					68 (350)	
	trans-12-Octadecenoic					60 (350)	
	Vaccenic				20 (368)		
$C_{18}H_{34}O_3$	*cis*-12-Hydroxy-9-octadecenoic (ricinoleic)				— (369)		— (171)
	trans-12-Hydroxy-9-octadecenoic (ricinelaidic)				— (369)		— (171)
$C_{20}H_{36}O_4$	α-9-Octadecene-1,18-dicarboxylic				74 (340)		
$C_{20}H_{38}O_2$	*n*-11-Eicosenoic			— (370)	40 (371, 372)		
$C_{22}H_{32}O_3$	Anacardic					57 (373)	
$C_{22}H_{38}O_6$	9,10-Diacetoxy-12-octadecenoic				— (344)		
$C_{22}H_{40}O_4$	Hendecenoic dimers				— (338)		
$C_{22}H_{42}O_2$	Brassidic	55 (357)			— (357)		
	Erucic	70 (171, 357)			58 (338, 357)		
$C_{30}H_{48}O_3$	α-Elemolic		— (374)				
$C_{11}H_{20}O_2$-$C_{22}H_{42}O_2$	Mixed unsaturated fatty acids from human hair fat					— (375)	

D. Alcohols

C_3H_6O	Allyl alcohol	— (6, 8)				80 (376)	
C_4H_8O	Crotyl alcohol	11 (377)					
C_5H_6O	2-Penten-4-yn-1-ol					42 (57, 60)	
$C_6H_{10}O$	Anhydro-[4-(enol)-acetobutyl]alcohol	47 (378, 379)					— (378)
$C_6H_{10}O_2$	2,3-Dihydroxy-1-propene (acetone compound)	— (380)					
$C_8H_{14}O$	4,5-Dihydroxy-2,6-octadiene	— (377)					
$C_8H_{16}O$	2,4,4-Trimethyl-1-penten-3-ol	— (40)					
$C_9H_9NO_3$	β-Nitrocinnamyl alcohol	80 (380*a*)					
$C_9H_{10}O$	Cinnamyl alcohol	78 (377)				17 (381)	
$C_{10}H_{12}O$	Methylstyrylcarbinol	— (382)					
$C_{10}H_{18}O$	Geraniol	— (6, 9, 191, 383)					
	Linaloöl	— (6, 9, 384)	80 (384)				
	1-Menthen-6-ol	— (385)					
$C_{10}H_{18}O_2$	1,4-Menthenediol	Good (200)					
$C_{10}H_{18}O_3$	Menthenetriol			— (386)			
$C_{10}H_{20}O$	Citronellol	— (383)					
$C_{12}H_{20}O_2$	Acetyllinaloöl	— (9)					
$C_{13}H_{26}O$	11-Hydroxy-1-tridecene	— (387)					
$C_{14}H_{26}O$	Methyldihydro-α-ionol		85 (388)				
$C_{14}H_{28}O$	11-Hydroxy-1-tetradecene	— (387)					
$C_{18}H_{32}O$	9,11,13-Octadecatrienol (elaeostearyl alcohol)				— (389)		
$C_{18}H_{36}O$	*cis*-9-Octadecenol (oleyl alcohol)	74–85 (3, 20, 354, 390, 391)		80 (1, 23)	60 (51, 361, 362, 364, 389)	50–100 (4, 169)	
	trans-9-Octadecenol (elaidyl alcohol)			— (391)			
$C_{18}H_{36}O_2$	*cis*-1,12-Dihydroxy-9-octadecene (ricinoleyl alcohol)				— (389)		
$C_{20}H_{30}O$	Vitamin A		— (392, 393)				
$C_{23}H_{30}O$	11-Hydroxy-11,11-diphenyl-1-hendecene	— (387)					
$C_{30}H_{50}O$	β-Amyrin	— (245, 246)					
	Skimmiene	— (394)					
$C_{30}H_{52}O$	Dihydrocuphol	— (395)					
$C_{32}H_{52}O$	Acetylskimmiol	— (396)					
$C_{40}H_{56}O$	Rubixanthin		— (397)				

TABLE I—*Continued*

ETHYLENIC COMPOUNDS OXIDIZED WITH ORGANIC PERACIDS

Ethylenic Compound		Yield of Oxirane, % (Reference)			Yield of α-Glycol, % (Reference)		
Formula	Name	Perbenzoic Acid	Monoperphthalic Acid	Peracetic Acid	Peracetic Acid	Performic Acid	Perbenzoic Acid
			E. Esters				
$C_4H_6O_2$	Vinyl acetate					— (376)	
$C_6H_{10}O_2$	Methyl 2,4-hexadienoate (sorbate)	— (398, 399)					
$C_6H_{10}O_3$	Ethyl acetoacetate	— (400)					
$C_8H_{12}O_2$	1-Acetoxy-1-cyclohexene	— (125)					
$C_9H_{14}O_2$	1-Acetoxy-3-methyl-1-cyclohexene	— (401)					
	2-Acetoxy-4-methyl-1-cyclohexene	— (125, 180)					
	Methyl diallylacetate	— (121)					
$C_{10}H_{16}O_4$	Diethyl allylmalonate		>32 (402)	32 (402)			
$C_{10}H_{18}O_2$	Methyl 2-nonenoate					50 (55)	
$C_{11}H_{12}O_2$	Cinnamyl acetate	70 (377)					
$C_{11}H_{18}O_2$	Methyl α-allocyclogeranate		65 (403)				
$C_{11}H_{18}O_4$	Diethyl (1-methyl-2-propenyl)malonate		51 (402)				
$C_{12}H_{20}O_2$	Ethyl α-cyclogeranate		60 (403)				
	Methyl 1,1,3-trimethyl-3-cyclohexene-2-acetate		60 (335)				
$C_{12}H_{20}O_3$	Ethyl 5-cyclopentyl-5-hydroxy-2-pentenoate					30 (404)	
$C_{12}H_{22}O_2$	Methyl 10-hendecenoate (undecylenate)	— (387)		40 (1, 23)	— (405)		
$C_{13}H_{20}O_4$	Diethyl diallylmalonate	— (121)					
$C_{13}H_{24}O_2$	Ethyl 10-hendecenoate (undecylenate)	— (387)			— (405)		
$C_{13}H_{24}O_3$	Ethyl 5-hydroxy-2-hendecenoate					20 (404)	
$C_{14}H_{24}O_4$	Dimethyl traumatate					— (55)	
$C_{14}H_{26}O_2$	Propyl 10-hendecenoate (undecylenate)				— (405)		
$C_{14}H_{26}O_3$	2-Methoxyethyl 10-hendecenoate (undecylenate)				— (405)		

$C_{17}H_{32}O_2$	Methyl palmitoleate				— (49)		
$C_{19}H_{34}O_2$	Methyl 9,12-octadecadienoate (linoleate)	25–40 (28, 29, 345, 406)		— (28, 29, 30)	<20 (345)		
	Methyl 9,11-octadecadienoate	20 (29, 310)					
$C_{19}H_{36}O_2$	Methyl *cis*-9-octadecenoate (oleate)	42–67 (3, 20)		45 (1, 23, 355)	50 (49, 72, 407)	96 (37,* 56)	
	Methyl *trans*-9-octadecenoate (elaidate)	— (171)		— (72)	— (49, 407)		
	Methyl *cis*-6-octadecenoate (petroselinate)	80 (408)			— (409)		
	Methyl *trans*-6-octadecenoate (petroselaidate)	— (408)					
$C_{19}H_{36}O_3$	Methyl hydroxyoleates					50 (56, 409*a*)	
	Methyl *cis*-12-hydroxy-9-octadecenoate (ricinoleate)	80 (29)		— (1, 23)		100 (4, 169)	
	Methyl *trans*-12-hydroxy-9-octadecenoate (ricinelaidate)	85–95 (28, 29)					
$C_{20}H_{34}O_2$	Ethyl 9,11,13-octadecatrienoate (eleostearate)				— (341)		
	Ethyl 9,12,15-octadecatrienoate (linolenate)	— (343)					
$C_{20}H_{38}O_2$	Ethyl *cis*-9-octadecenoate (oleate)	— (171, 240, 342, 343)		40 (410)	— (29, 51, 361, 362)		
	Ethyl *trans*-9-octadecenoate	— (240)			— (29)		
	Oleyl acetate			— (355)			
$C_{21}H_{32}O_2$	Methyl (+)-pimarate	— (411)	— (412)				
$C_{21}H_{34}O_2$	Methyl (+)-dihydropimarate	— (411)					
$C_{23}H_{44}O_2$	Methyl brassidate	— (357)			Good (357)		
	Methyl erucate	75 (357)			— (357)		
$C_{26}H_{50}O_2$	Octyl oleate					— (37)	
$C_{31}H_{50}O_3$	Methyl α-elemolate		— (374)				
$C_{32}H_{52}O_2$	β-Amyrin acetate			— (413)			
	Euphadienyl acetate	— (247)					
	Euphorbadienyl acetate	— (414)					
	Euphol acetate	— (395)					
	Germanicol acetate	— (415)					
	Lanosteryl acetate	— (416, 417)					
	Taraxerol acetate		— (418)				
$C_{32}H_{54}O_2$	Artenyl acetate			— (418*a*)			
	Euphenyl acetate	— (247)					

TABLE I—*Continued*

ETHYLENIC COMPOUNDS OXIDIZED WITH ORGANIC PERACIDS

Ethylenic Compound		Yield of Oxirane, % (Reference)			Yield of α-Glycol, % (Reference)		
Formula	Name	Perbenzoic Acid	Monoperphthalic Acid	Peracetic Acid	Peracetic Acid	Performic Acid	Perbenzoic Acid
			E. Esters—Continued				
$C_{32}H_{54}O_2$	Euphorbenyl acetate	— (247)					
(*Cont'd*)	Isodihydrocuphol acetate	70 (420)					
	Tirucallenyl acetate	— (247)					
$C_{33}H_{52}O_4$	Methyl acetyleburicoate	— (421)					
$C_{36}H_{68}O_2$	Oleyl oleate			— (355)			
$C_{37}H_{56}O_2$	Artenyl benzoate	— (418*a*)					
$C_{38}H_{56}O_9$	Escingenin tetraacetate		— (422)				
$C_{39}H_{72}O_4$	Propylene glycol dioleate					— (37)	
$C_{40}H_{58}O_{10}$	Isoescingenin pentaacetate		— (423)				
$C_{40}H_{74}O_5$	Diethyleneglycol dioleate			— (355)			
$C_{44}H_{60}O_3$	Cryptoxanthin diacetate		— (424)				
$C_{44}H_{60}O_4$	Xanthophyll diacetate		6 (425)				
	Zeaxanthin diacetate		— (425)				
$C_{44}H_{62}O_5$	Capsanthin diacetate		— (426)				
$C_{57}H_{104}O_6$	Triolein			86 (1, 427)			
	Butyl Carbitol esters of unsaturated fatty acids			— (355)			
	Castor oil			73 (1, 427)	36 (52, 361, 362, 369, 428)		
	Cocoa butter				— (50)		
	Coconut oil				— (428)		
	Corn oil			70–80 (1, 427, 429)			
	Cottonseed oil			71 (1, 427)			
	Lard oil			74 (1, 427)			
	Linseed oil			66 (1, 427)			
	Menhaden oil			57 (1, 427)			
	Methyl esters of soybean oil acids			— (355)			
	Methyl esters of unsaturated acids			— (355)			
	Neatsfoot oil			77 (1, 427)			
	Olive oil			81 (1, 427)	— (428)		
	Peanut oil			75 (1, 427)			
	Perilla oil			64 (1, 427)			
	Rapeseed oil			71 (1, 427)			
	Rice oil				— (419)		
	Sardine oil					— (430)	
	Soybean oil			67–75 (1, 427, 429)	— (431-436)	— (37,* 434)	
	Tall oil				— (358, 437)		
	Tallow				— (50)		
	Tobaccoseed oil			73 (1, 427)			
			F. Aldehydes and Ketones (including carbohydrate derivatives)				
$C_6H_{10}O_3$	Rhamnal						75 (438, 439)
$C_6H_{10}O_4$	Galactal						— (440)
	Glucal	— (438, 439)					— (438, 441)
$C_7H_{12}O_4$	3-Methylglucal						30 (442)
$C_8H_{14}O$	Methylheptenone	— (8)					
$C_{10}H_{10}O$	Benzylideneacetone	— (9)					
$C_{10}H_{16}O$	Citral	— (6, 9)					
	Pulegone	59 (443)					
$C_{10}H_{18}O$	Citronellal	— (6, 8)					
$C_{12}H_{16}O_7$	Triacetylgalactal						33 (440)
	Triacetylglucal						30 (441, 442)
$C_{12}H_{20}O_9$	Lactal						— (444)
	Cellobial						90 (439)
$C_{13}H_{20}O$	α-Ionone	96.5 (445)	— (446)				
	β-Ionone	86 (445)	60–70 (446)				
$C_{13}H_{22}O$	α-Dihydroionone		50 (447)				

* Oxirane formed

TABLE I—*Continued*

ETHYLENIC COMPOUNDS OXIDIZED WITH ORGANIC PERACIDS

Ethylenic Compound		Yield of Oxirane, % (Reference)			Yield of α-Glycol, % (Reference)		
Formula	Name	Perbenzoic Acid	Monoperphthalic Acid	Peracetic Acid	Peracetic Acid	Performic Acid	Perbenzoic Acid
	F. Aldehydes and Ketones (including carbohydrate derivatives)—Continued						
$C_{13}H_{24}O$	11-Keto-1-tridecene	— (387)					
$C_{14}H_{18}O_9$	Tetraacetyl-1-glucosene						30 (448)
$C_{14}H_{22}O$	Methyl α-ionone		60 (445)				
$C_{14}H_{26}O$	11-Keto-1-tetradecene	45–55 (387)					
$C_{15}H_{26}O_2$	α-Dihydroionone ethylene ketal		85 (449)				
$C_{17}H_{24}O$	11-Keto-11-phenyl-1-hendecene	— (387)					
$C_{30}H_{48}O$	Lanostenone	— (416)					
$C_{30}H_{50}O$	Euphenone	— (247)					
	G. Ethers						
C_4H_4O	Furan						— (450)
C_4H_8O	Ethyl vinyl ether	25 (451)					
C_5H_8O	5,6-Dihydro-1,2-pyran	58 (452)					
$C_6H_{10}O$	Diallyl ether	— (121)				71 (453)	
$C_6H_{10}O_2$	2-Propenyldioxolane	45 (170)					
$C_9H_{10}O$	Phenyl allyl ether	35 (454)					
$C_9H_{16}O_3$	α,α′-Diallylglycerol					25–33 (455)	
$C_{10}H_{10}O_2$	Isosafrole	— (203)			100 (138)		
	Safrole				— (138)		
$C_{10}H_{12}O$	Anethole			62 (24)	55–100 (32, 138)		— (456)
	Methyl cinnamyl ether	85 (377, 457)					
$C_{10}H_{12}O_2$	Eugenol				100 (138)		
	Isoeugenol			— (32)			
$C_{11}H_{14}O$	Ethyl cinnamyl ether	— (457)					
$C_{12}H_{14}O$	Allyl cinnamyl ether	50 (454)					
$C_{12}H_{14}O_2$	Hydroquinone diallyl ether	25 (454)					
$C_{14}H_{22}O$	Dispiro[dicyclohexane-2,5-dihydrofuran]	60 (458)					
$C_{22}H_{36}O$	Cardanol methyl ether					95 (459)	
	H. Miscellaneous						
$C_4H_6O_2S$	Butadiene sulfone				— (460)		
$C_5H_8O_2S$	β-Isoprene sulfone				60 (460)		
$C_6H_{10}O_2S$	Dimethylbutadiene sulfone				— (460)		
$C_7H_{13}NO$	2-Ethyl-2-pentenamide		— (461)				
$C_8H_{15}NO$	2-Ethyl-2-hexenamide		69 (461)				
	2-Propyl-2-pentenamide		85 (461)				
$C_9H_{10}O_3$	Furfural diacetate	8 (462)					
$C_{10}H_{12}O_2S$	Benzyl propenyl sulfone				— (460)		
$C_{11}H_{10}N_2O$	Furfuralphenylhydrazone	30 (463)					
$C_{11}H_{12}N_2S$	Thiopyrine	— (464)					
$C_{13}H_{12}N_2$	Benzaldehydephenylhydrazone	60 (463)					
$C_{15}H_{20}O_4$	ψ-Santonin	— (339)					
$C_{18}H_{35}NO$	Oleamide			65 (465, 466)			
$C_{19}H_{37}NO$	N-Methyloleamide			38 (465, 466)			
$C_{20}H_{37}NO_2$	N-Acetyloleamide			29 (465, 466)			
$C_{20}H_{39}NO$	*n*-11-Eicosenamide					— (370)	
$C_{20}H_{39}NO_2$	N-(2-Hydroxyethyl)oleamide			59 (465, 466)			
$C_{24}H_{39}NO$	N-Phenyloleamide			45 (465, 466)			
$C_{24}H_{47}NO$	N-(*n*-Hexyloleamide)			53 (465, 466)			
$C_{27}H_{27}NO_4$	α-Phellandrene-β-naphthol adduct (*p*-nitrobenzoate)	90 (467)					
$C_{28}H_{41}NO$	N-(α-Naphthyl)oleamide			— (466)			
$C_{28}H_{55}NO_2$	N-(*n*-Decyl)oleamide			89 (465, 466)			
$C_{30}H_{59}NO_2$	N-(*n*-Dodecyl)oleamide			45 (465, 466)			
	N-Amylamides of unsaturated fatty acids			— (355)			
	N,N-Dibutylamides of unsaturated fatty acids			— (355)			

Addendum to Table I

The compounds appearing in this addendum are listed alphabetically in sections which correspond to those in Table I.

Compound	Peracid	Product	Yield	Reference
A. Hydrocarbons and Substituted Hydrocarbons				
3-Acetoxy-1-cyclohexene	Peracetic, performic	Triol	20–25	468
α-Amyrene	Peracetic	Oxirane	—	469
1-(2-Biphenyl)-3,4-dihydronaphthalene	Monoperphthalic	Oxirane	—	470
α-Cyclohexylideneethylbenzene	Performic	Glycol	42	471
α-Cyclohexylstyrene	Performic	Glycol	42	471
3-Methoxy-1-cyclohexene	Peracetic	Glycol	30	468
1-Phenyl-1-(2-biphenylyl)ethylene	Perbenzoic	Aldehyde (via the oxirane)	—	470
B. Steroids				
3β-Acetoxy-7,8-epoxy-9(11),22-ergostadiene dibromide	Perbenzoic	Glycol	—	472
3β-Acetoxy-7,9(11),20-ergostatriene	Perbenzoic	Oxirane	—	472
3β-Acetoxy-7,9,22-ergostatriene	Monoperphthalic	Oxirane	—	473
16,20(22)-Allofurostadiene-3β,26-diol diacetate	Monoperphthalic	Oxirane	—	474
Allopregnane-11,20-dienol acetate	Perbenzoic	Glycol	—	475
8(14)-Androsten-3β,17β-diol diacetate	Monoperphthalic	Oxirane	10–35	476
9-Androsten-3α-ol-17-one	Perbenzoic	Oxirane	—	477
3β-Benzoxy-7,9(11)-cholestadiene	Monoperphthalic	Oxirane	70	478
3β-Benzoxy-7-cholestene	Monoperphthalic	Oxirane	50	478
2-Cholesten-6-one	Perbenzoic	Oxirane	—	479
3β,17β-Diacetoxy-7,9(11)-androstadiene	Monoperphthalic	Oxirane	40	478
22,23-Dibromo-3β-acetoxy-7,9(11)-ergostadiene	Peracetic	Oxirane	—	472
7,9(11),22-Ergostatrien-3β-ol acetate	Perbenzoic	Oxirane	—	480
9-Etiocholen-3α-ol-17-one	Perbenzoic	Oxirane	—	477
Methyl 3α-acetoxy-7,9-choladienate	Monoperphthalic	Oxirane	—	473
Methyl 3α-hydroxy-9(11)-cholenate	Perbenzoic	Oxirane	—	481
5β-Methyl-3β-methoxy-19-norcoprost-9(10)-en-6-one	Peracetic	Oxirane	—	482
5β-Methyl-19-norcoprost-9(10)-en-3β,6β-diol diacetate	Peracetic	Oxirane	—	482
9(11),17(20)-Pregnadiene-3α,11,20-triol triacetate	Perbenzoic	Oxirane	—	483
9(11)-Tigogenin acetate	Perbenzoic	Oxirane	—	481
C. Acids				
cis-9-Hendecenoic	Performic	Glycol	30	484
trans-9-Hendecenoic	Performic	Glycol	55	484

Addendum to Table I—*Continued*

Compound	Peracid	Product	Yield	Reference
E. Esters				
α-Amyrin acetate	Peracetic	Oxirane	20	469
α-Amyrin benzoate	Peracetic	Oxirane	50	469
cis-2-Buten-1,4-diol diacetate	Peracetic	Tetraacetate	57	485
trans-2-Buten-1,4-diol diacetate	Peracetic, performic	Tetraacetate, formates	51–79	485
Methyl acetyleburicoate	Perbenzoic	Oxirane	--	486
Methyl morolate acetate	Perbenzoic, peracetic	Oxirane	80	487
Methyl morolate benzoate	Peracetic	Oxirane	—	487
Moradiol diacetate	Peracetic	Oxirane	—	487
α-Noramyrenonyl acetate	Perbenzoic	Oxirane	—	488
Peach oil	Peracetic	Not isolated	—	489
Zeorinin acetate	Peracetic	Oxirane	—	490
Zeorinin benzoate	Peracetic	Oxirane	—	490
G. Ethers				
Butyl *p*-(2-methylalloxy)benzoate	Peracetic	Glycol	50	491
m-Carbobutoxyphenyl 2-methallyl ether	Peracetic	Glycol	—	491
4-Chloro-3-methylphenyl 2-methallyl ether	Peracetic	Glycol	50	491
p-Chlorophenyl 2-methallyl ether	Peracetic	Glycol + oxirane	—	491
3,5-Dimethylphenyl 2-methallyl ether	Peracetic, performic	Glycol	6–50	491
2-Methallyl *m*-nitrophenyl ether	Peracetic	Glycol	33	491
2-Methallyl phenyl ether	Peracetic	Glycol + oxirane	42 + 25	491
2-Methallyl *m*-tolyl ether	Peracetic, performic	Glycol	6–25	491
2-Methallyl *o*-tolyl ether	Peracetic	Glycol + oxirane	20	491
2-Methallyl *p*-tolyl ether	Peracetic	Glycol + oxirane	—	491
5,6-Dihydro-2-pyran	Performic	Glycol	60	492
2,5-Dihydro-2,2,5,5-tetramethylfuran	Performic	Oxirane	25	492
H. Miscellaneous				
2-Methallyl chloride	Peracetic	Glycol	—	491

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