ORGANIC PERACIDS

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I. Introduction

Organic peracids are a relatively new class of organic compounds (30, 31, 33, 172, 173, 174, 175, 176, 177, 182, 183, 184, 185, 186, 187, 188, 189, 224, 399) and within the past several decades a large number of publications have appeared which describe their preparation, properties, and use as oxidizing agents for organic compounds. The activity in this field is not unexpected, since for many applications, particularly in the preparation of oxirane compounds and glycols from unsaturated substances (22, 23, 85, 88, 96, 104, 111, 217, 232, 262, 265, 425, 428, 429, 430, 431, 479, 480, 486, 505, 506, 508) (Section III A and tables 1, 2, 3,

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and 4), organic peracids have numerous advantages over classical inorganic oxidizing agents, such as permanganates, dichromates, chlorates, nitric acid, and hypochlorites. In fact, oxidation with organic peracids represents the only efficient way of preparing some long-chain α-glycols and oxirane compounds.

Oxidations with organic peracids are usually conducted in homogeneous solution and often proceed rapidly under mild reaction conditions with a minimum of side reactions and by-product formation, and the oxidation products are readily isolable in a high degree of purity and in high yield. Since many oxidations with aliphatic peracids are conducted in a solution of the corresponding organic acid, and since the peracid is converted to the organic acid as a result of the oxidation, the solvent may be readily recovered in a pure state for re-use, and the oxidation product obtained as a distillation residue for further processing. Furthermore, some of the more important aliphatic peracids, such as performic and peracetic acids, as well as the carboxylic acids corresponding to them, are soluble both in water and in organic media, thereby affording a wide flexibility in the choice of solvent or solvent mixture for the reaction. When the oxidation product is insoluble in water and the peracid and its corresponding acid are soluble, the oxidation product can usually be isolated in a simple manner by pouring the reaction mixture into water and separating the product mechanically.

Oxidations with organic peracids also lend themselves readily to quantitative and kinetic study (74, 75, 86, 87, 89, 98, 111, 114, 115, 116, 119, 122, 124, 249, 302, 333, 345, 346, 357, 487, 499, 500, 501, 545, 580) (Sections IV and V), since unconsumed peracid can be rapidly determined iodimetrically at suitable time intervals. If desired, a correction can be made in the final yield for the small quantity of product lost as a result of the analyses. Thus it is not only possible to obtain valuable kinetic data as well as a desired product from a single experiment, but by plotting the consumption of peracid against time it is also possible to determine the optimum reaction time for a given temperature with a minimum of effort.

In contrast, many of the classical inorganic oxidizing agents are frequently converted to voluminous and difficult-to-handle end products, such as manganese dioxide from potassium permanganate, or complex mixtures of oxidation products are obtained, as is usually the case in nitric acid or hypochlorite oxidations, thereby rendering isolation of the desired products extremely tedious or impossible. In oxidations with inorganic oxidants, the greatest problem is not to effect the oxidation but to isolate the reaction products in a sufficiently pure state for identification. Also, the need for operating in aqueous media seriously limits the usefulness of some inorganic oxidants for organic reactions. Furthermore, the impossibility or difficulty of following the course of the reaction quantitatively often requires that numerous experiments be conducted and that the products be separated and purified in order to determine the important variable of time.

No discussion of organic peracids can be complete without mentioning the important oxidizing agent hydrogen peroxide. This substance, which is available commercially in aqueous solutions containing from about 3 to 90 per cent hydrogen peroxide, is fairly stable, it has a low equivalent weight, and its reduction

product is water. These characteristics make it extremely attractive as an oxidant for organic reactions, but its relatively high price on an active oxygen basis, its immiscibility with many organic compounds, and the unavailability of its active oxygen for preparative purposes have restricted its large-scale use for organic syntheses. Its low equivalent weight, however, compensates for the high price of the active oxygen, especially when high-molecular-weight compounds are to be oxidized, and in recent years several noteworthy attempts have been made to overcome the other disadvantages and make hydrogen peroxide more generally applicable (56a, 352, 353, 354, 355, 356, 358, 364, 365, 366, 532, 533, 534, 535, 546). Perhaps the most satisfactory technique, however, for utilizing the oxidizing capacity of hydrogen peroxide efficiently in organic reactions is to convert the active oxygen to the peracid form. Organic peracids can be readily prepared, usually with little loss of oxygen, by treating organic acids, acyl halides, or acid anhydrides with 25–100 per cent hydrogen peroxide or with inorganic peroxides (21, 22, 33, 91, 97, 122, 123, 172, 181, 182, 183, 184, 185, 186, 188, 189, 205, 211, 212, 215, 216, 217, 233, 236, 239, 240, 241, 242, 271, 301, 360, 362, 398, 448, 449, 450, 452, 486, 495, 525). In many cases the peracid need not be isolated; it is sufficient to dissolve the substance to be oxidized in the organic acid or anhydride and add the hydrogen peroxide (4a, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 24, 35, 45a, 46, 57, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 70, 70a, 71, 120, 121, 125, 154, 155a, 159, 163a, 168, 169, 170, 171, 171a, 193, 196, 199, 202, 204, 222, 223, 223a, 228, 229, 231, 232, 235, 245a, 251, 252, 253, 254, 255, 256, 257, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 274, 297, 298, 300, 331a, 331b, 333a, 336a, 337, 340a, 342, 351, 386, 388, 389, 390a, 393, 395, 400, 403, 404, 405, 406, 412, 418, 421, 422, 423, 424, 434, 443, 457, 460, 461, 463, 477a, 483, 489, 490, 491, 492, 505, 506, 509, 524, 525, 537, 538, 541, 551, 552, 557). As the peracid forms, it is consumed, and since formation of peracid is an equilibrium reaction, peracid will continue to form and be consumed until very little oxidizable substance remains. Under certain conditions, loss of peroxide can be held to a minimum and substantially stoichiometric utilization of the active oxygen can be effected and quantitative yields of product obtained (505, 506). This *in situ* preparation and consumption of peracids is the technique most frequently employed in oxidations involving aliphatic peracids. By operating either in this manner or by isolating the peracid, which is sometimes necessary since the reaction conditions or the peracid being utilized may not be suitable for the *in situ* technique, the remaining disadvantages of hydrogen peroxide appear to be obviated.

II. Preparation and Properties of Organic Peracids

A. ALIPHATIC PERACIDS

1. Performic acid

Performic acid was apparently first prepared by D'Ans and coworkers (182, 184, 185, 189), who treated approximately 98 per cent hydrogen peroxide with formic acid in the presence of 1 per cent of sulfuric acid as catalyst. The reaction

is reversible, contrary to the opinion of Clover and Richmond (173) regarding peracids in general, and equilibrium is reached within 2 hr. (equation 1).

$$HCO_2H + H_2O_2 \rightleftarrows HCO_3H + H_2O \quad (1)$$

Equilibrium constants for this reaction have been determined by D'Ans and Frey (185) and by Hatcher and Holden (241). Other catalysts that may be employed are nitric, hydrofluoric, and phosphoric acids, and inorganic salts, such as potassium nitrate, ammonium sulfate, sodium bisulfate, sodium phosphite, and barium nitrate. When equimolar proportions of reactants are employed, solutions containing about 48 per cent performic acid are obtained. By employing a 75 per cent excess of hydrogen peroxide and higher proportions of sulfuric acid, and fractionally distilling the equilibrium mixture under vacuum,[2] D'Ans and Kneip (189) obtained solutions containing up to 90 per cent performic acid. Koch and Maisin (301) also prepared performic acid substantially by the procedure of D'Ans, but they employed ether solutions of hydrogen peroxide. Recently Greenspan (233), duplicating the work of D'Ans and Frey (184, 185), employed 90 per cent as well as 30 per cent hydrogen peroxide, and obtained 35.8 per cent and 4.7 per cent solutions of performic acid, respectively. Attainment of equilibrium requires 30 min. when 90 per cent hydrogen peroxide is employed and 2 hr. with the less concentrated hydrogen peroxide. In view of the convenience and greater safety of 30 per cent hydrogen peroxide, as compared with the 90 per cent solution (45), the work of Toennies and Homiller (525) and of Swern and Findley is of interest (507). These investigators employed 30 per cent hydrogen peroxide and extremely large molar excesses (20 or 30:1) of 88–100 per cent formic acid to accelerate attainment of equilibrium, and they demonstrated that equilibrium is reached in less than 1 hr. No catalyst is necessary.

It has also been reported that performic acid is formed when formic acid is treated with oxygen in the presence of unfiltered ultraviolet radiation (164).

Pure performic acid has apparently never been prepared. The 90 per cent solution, however, is a colorless liquid with a characteristic odor. The vapor of performic acid is extremely irritating to the mucous membranes and produces painful inflammations of the skin. It is soluble in water, ethyl alcohol, diethyl ether, chloroform, benzene, and other organic solvents. D'Ans and Kneip (189) have reported that the peracid is more volatile than formic acid. Its solutions are unstable (189, 233, 507, 525), the 90 per cent solution losing 25 per cent of its active oxygen when stored for 24 hr. at 0°C.; the main products of decomposition are carbon dioxide and water (189). At 60° and 80°C. performic acid loses its active oxygen at a very rapid rate, with liberation of carbon dioxide (204). Concentrated solutions of performic acid (60 per cent or higher) can be caused to explode violently by the addition of small quantities of catalysts, such as zinc dust, lead dioxide, red lead, and sodium azide, the first two causing even the 45 per cent strength to explode (189). Numerous other substances cause performic acid solutions to decompose at rates ranging from slow decomposition to detona-

[2] This is a hazardous procedure, and adequate precautions should be taken to protect the operator.

tion (189). In the absence of catalysts, performic acid explodes when heated rapidly to 80–85°C.

Performic acid reacts rapidly with aqueous solutions of potassium iodide, liberating iodine. This reaction has been employed by Toennies and Homiller for the quantitative determination of performic acid (523a, 525). Performic acid shows typical peroxide properties, such as bleaching dye solutions and reacting with aqueous potassium permanganate.

It has been reported that the incidence of benzopyrene cancer in mice is greatly decreased by one or more injections of 0.1 mg. or less of performic acid (338).

2. Peracetic acid

More work has been published on the preparation of peracetic acid than on that of any other organic peracid. In the first investigations the peracid was not isolated, but was obtained in dilute aqueous solutions by mild hydrolysis of benzoyl acetyl peroxide (221, 399) and diacetyl peroxide (173, 399), by treatment of diacetyl peroxide with alkali followed by acidification (399), and by reaction of diacetyl peroxide or acetic anhydride with dilute hydrogen peroxide solutions (172). A few years later, D'Ans and Friederich (187) treated diacetyl peroxide with concentrated or anhydrous hydrogen peroxide and obtained concentrated solutions of peracetic acid. In a continuation of this work, D'Ans and coworkers treated substantially anhydrous hydrogen peroxide with an equimolar quantity of acetyl chloride (181, 183, 186, 188), acetic acid (182, 184, 185), or acetic anhydride (182, 184, 185, 189). The reaction of acetyl chloride with hydrogen peroxide is better suited for the preparation of acetyl peroxide than peracetic acid, and therefore the last two techniques have completely superseded it for the laboratory preparation of peracetic acid.

When a mixture of equimolar quantities of acetic acid and 98 per cent hydrogen peroxide to which 1 per cent of sulfuric acid has been added is allowed to stand at 14.6°C. until equilibrium is attained (12–16 hr.), a solution containing 50 per cent peracetic acid is obtained (184). When acetic anhydride is employed instead of acetic acid (182, 184, 185), similar results are obtained but in a much shorter time, and when 2 moles of hydrogen peroxide are employed for each mole of acetic anhydride, solutions containing 70 per cent peracetic acid are obtained directly. The equilibrium constants for these reactions have been studied by D'Ans and Frey (185), Hatcher and Holden (241), and Paillard and Briner (397). An excess of acetic anhydride should be avoided to prevent conversion of the peracetic acid to the highly explosive diacetyl peroxide. Vacuum distillation[3] of the 70 per cent solution of peracetic acid yields a fraction, in good yield, containing as much as 90 per cent peracetic acid. Redistillation of fractions containing at least 85 per cent peracetic acid, followed by fractional freezing and centrifuging, yields pure peracetic acid (184).

Although numerous other investigators (21, 22, 91, 97, 205, 217, 233, 236, 240, 241, 448, 449, 450, 452, 486) have studied the reaction of hydrogen peroxide with

[3] See footnote 2.

acetic acid or anhydride, only minor improvements have been made in the original procedures of D'Ans and his colleagues. Thus, Erlenmeyer (205) reported that it is better to add the hydrogen peroxide to the acetic anhydride–sulfuric acid mixture. Böeseken and coworkers (91, 97) claimed that peracetic acid solutions free of diacetyl peroxide can be obtained by treating acetic anhydride with 45–50 per cent hydrogen peroxide and employing *p*-toluenesulfonic acid as catalyst. They also pointed out that the stability of the peracetic acid solution is improved by vacuum distillation, which should be carried out in the dark. Smit (486) found that 30 per cent hydrogen peroxide can be employed instead of highly concentrated or anhydrous hydrogen peroxide. Grundmann and Trischmann (236) also employed 30 per cent hydrogen peroxide and emphasized that the reaction temperature should not be too low during the addition of the reactants; otherwise complete mixing may occur before any reaction has taken place, at which point the reaction may proceed with explosive violence. Findley, Swern, and Scanlan (217) treated acetic anhydride with 25–30 per cent hydrogen peroxide and found that a catalyst is unnecessary. The reaction temperature employed by these investigators was 40°C., and yields as high as 90 per cent were obtained (503).

Peracetic acid can also be prepared by the direct oxidation of acetaldehyde with oxygen. The Consortium für Elektrochemische Industrie (174, 175, 176) and Galitzenstein and Mugdan (224) demonstrated that peracetic acid is formed when freshly distilled dry acetaldehyde is treated with oxygen at $-10°$ to $-20°$C. in the liquid phase. The oxygen absorption rate is considerably accelerated when the reaction mixture is irradiated with ultraviolet light. Manganese salts and water must be rigorously excluded, but salts of cobalt, chromium, iron, uranium, and vanadium may be employed as catalysts (175, 177, 224, 562). Inert solvents, such as acetic acid or ethyl acetate, may also be employed (309). The unreacted acetaldehyde is removed by distillation at low temperatures, yielding as a residue peracetic acid containing some acetic acid. While unreacted acetaldehyde is present in the mixture, the temperature must not be allowed to rise to room temperature; otherwise a violent oxidation of acetaldehyde to acetic acid occurs, with concomitant destruction of the peracetic acid. Although the oxygen oxidation of liquid acetaldehyde gives fair yields of peracetic acid, Bloomfield and Farmer (72) reported that in a large-scale operation a violent explosion resulted.

Vapor-phase oxidation of acetaldehyde under proper conditions may also be employed to prepare peracetic acid (73, 79, 151, 197a, 243, 391, 392), but such oxidations are employed mainly in the preparation of acetic acid from acetaldehyde. It has been pointed out that not more than 30 per cent of the oxygen theoretically necessary to convert the aldehyde to the peracid should be employed (73, 151).

The direct oxygen oxidation of acetaldehyde under a variety of conditions has been the subject of many investigations (1, 78, 79, 130, 131, 244, 246, 299, 332, 333, 391, 402, 459, 562, 570, 571) in which the kinetics and mechanism of the oxidation, rather than the preparation and isolation of the peracetic acid, were

studied. Peracetic acid is formed as an intermediate during the oxidation of acetaldehyde to acetic acid, and under certain conditions the peracid can be made the main product.

Other procedures for the preparation of peracetic acid consist in the reaction of acetic acid with oxygen in the presence of unfiltered ultraviolet radiation (165), the reaction of acetic acid with ozone (397), the reaction of ketene with hydrogen peroxide (184), the reaction of acetaldehyde with ozone–oxygen mixtures (143, 144, 219), the reaction of aqueous sodium perborate with acetic anhydride (495), and the reaction of boric–acetic anhydride with hydrogen peroxide (184). The last-named reaction produces peracetic acid in 79 per cent yield, whereas the reaction of acetic acid with oxygen or ozone yields only small quantities of peracetic acid. In the reaction of ketene with hydrogen peroxide, the peracetic acid which forms is rapidly converted to diacetyl peroxide by further reaction with ketene. In the reaction of acetaldehyde with ozone–oxygen mixtures, it is the oxygen which converts the aldehyde to the peracid; the ozone serves only as a catalyst (140, 142, 145). Thus, in the reaction of benzaldehyde–oxygen–ozone mixtures, the yield of perbenzoic acid decreases as the oxygen content decreases, and in the absence of oxygen no peracid is formed. The rate of absorption of oxygen by benzaldehyde, however, is increased by the presence of one part of ozone in ten million parts of oxygen (146, 147).

Pure peracetic acid, $d_{4^\circ}^{15^\circ} = 1.226$, is a colorless liquid which melts at 0.1°C. (184). Its boiling point has been reported as 20–30°C. at 10–20 mm. (184), 25°C. at 12 mm. (21), 35–36°C. at 29 mm. (22), and 105°C. (156). It is readily soluble in water, ethyl alcohol, diethyl ether, sulfuric acid, acetic acid, and other organic solvents (156). It has an intensely sharp odor, and it reacts strongly with cork, rubber, and the skin (184). It has bactericidal (312) and bleaching properties (163), in common with other peracids and peroxides in general.

Peracetic acid is reported to be insensitive to impact (156), but it explodes violently when heated at 110°C. (184). The region of explosive decomposition of mixtures of oxygen and peracetic acid has been investigated (1). When peracetic acid is heated at 130°C. in a bomb, it explodes, yielding methane, ethane, ethylene, methyl alcohol, and carbon dioxide, and when heated at 150°C. in an atmosphere of ammonia it is converted to methylamine, methyl alcohol, and oxygen (213). Hatcher and Toole (245) reported that peracetic acid decomposes when heated, forming carbon dioxide, formic acid, and glycolic acid. It is slowly decomposed by platinum black at room temperature, and it is rapidly hydrolyzed to acetic acid and hydrogen peroxide by aqueous sodium hydroxide (119). Manganese salts also catalyze the decomposition of peracetic acid, the products being acetic acid, carbon dioxide, carbon monoxide, and oxygen (333). In the absence of catalysts, concentrated solutions of peracetic acid are fairly stable at room temperature (15°C.), 87–95 per cent solutions remaining virtually unaltered on standing for about 5 weeks (189). In this respect, peracetic acid differs markedly from performic acid, which is unstable. D'Ans and Kneip (189) reported that a 50 per cent solution of peracetic acid shows no loss of peracid after storage for 14 days, and Greenspan (233) reported that a 45 per cent

solution retains 75 per cent of the peracid after 49 days. Solutions stabilized with one hundred parts per million of sodium pyrophosphate contain 94 per cent of the peracid after 49 days' storage (233). Other inorganic and organic stabilizers for peracids have also been suggested (377, 451). Five to ten per cent solutions of peracetic acid in acetic acid, however, show significant oxygen losses at room temperature but very little oxygen loss when stored at 0–5°C. (217).

A 40 per cent solution of peracetic acid in acetic acid is sold commercially (156), and information is available regarding the stability, flammability, pH, flash point, solubility, specific gravity, and conditions for the storage and handling of this solution.

Procedures for the analytical determination of peracetic acid in the presence of hydrogen peroxide and diacetyl peroxide have been described (34, 184, 241, 486).

Ethyl peracetate has been reported (32). This compound cannot be classed as a derivative of peracetic acid and ethyl alcohol, but rather as a derivative of acetic acid and ethyl hydroperoxide (363, 569).

3. Perpropionic acid

Dilute solutions of perpropionic acid have been prepared from propionyl peroxide by mild aqueous hydrolysis (173) or by treatment with aqueous hydrogen peroxide (172), and also by the reaction of propionic acid with 30 per cent hydrogen peroxide (271). Concentrated solutions have been prepared by D'Ans and coworkers (182, 184) by treating propionic acid or its anhydride with approximately 100 per cent hydrogen peroxide. Equilibrium constants for these reactions have been reported by D'Ans and Frey (185). When equimolar proportions of propionic acid and hydrogen peroxide, to which 1 per cent of sulfuric acid has been added as catalyst, are allowed to stand at 14.8°C. for about 12–16 hr., a solution containing about 55 per cent of perpropionic acid is obtained directly. When 1 mole of propionic anhydride is treated with 2 moles of hydrogen peroxide at room temperature (sulfuric acid catalyst) until equilibrium is attained, and the reaction mixture is then distilled under vacuum,[4] fractions containing up to 89 per cent perpropionic acid are isolated in good yield. By fractional freezing and centrifuging, perpropionic acid of 99.5 per cent purity is obtained.

Perpropionic acid has also been prepared from propionaldehyde by oxygen oxidation in the liquid phase at low temperatures (174, 175, 176, 177, 224, 570) in an analogous manner to the preparation of peracetic acid from acetaldehyde. The same catalysts are suitable, and the same precautions must be observed (dry oxygen, absence of manganese salts, etc.). Steacie and coworkers (497) studied the oxygen oxidation of propionaldehyde at 120–170°C. and reported that perpropionic acid is formed as an intermediate, although it was not isolated. Newitt and coworkers (391, 392) also studied the vapor-phase oxidation of propionaldehyde and reported that aqueous solutions of the oxidation products contain perpropionic acid, as well as a peroxide isomeric with it. Recently it has been shown that peracids, including perpropionic acid, can be obtained by the vapor-phase oxidation of aldehydes, provided that not more than 30 per cent of

[4] See footnote 2.

the oxygen theoretically necessary to convert the aldehyde to the peracid is employed (73, 151).

Perpropionic acid can also be prepared by treating propionaldehyde in hexane or carbon tetrachloride solution with ozone–oxygen mixtures (143).

When propionic acid is treated with oxygen in the presence of unfiltered ultraviolet radiation, the peracid is formed (165). Its rate of formation under these conditions is much greater than that of peracetic acid when acetic acid is similarly treated.

Pure perpropionic acid has also been prepared in good yield by treating boric–propionic anhydride with hydrogen peroxide (184).

Perpropionic acid is analogous to peracetic acid in its physical and chemical properties. Its melting point is −13.5°C. (184). It is more stable and less explosive than peracetic and performic acids, and on heating it deflagrates (184, 212). When heated in a steel autoclave it is converted to carbon dioxide, ethylene, ethane, and methane; at moderate temperatures it is converted to ethyl alcohol and carbon dioxide (212).

4. Perbutyric acid

Perbutyric acid has been prepared by the reaction of butyric acid or butyric anhydride with hydrogen peroxide (182, 184, 271). Equilibrium constants for these reactions have been reported by D'Ans and Frey (185). By vacuum distillation,[5] followed by fractional freezing and centrifuging, 95.4 per cent perbutyric acid has been obtained (184).

Perbutyric acid has also been prepared by the reaction of butyraldehyde with ozone–oxygen mixtures (143, 145, 148, 149, 150, 219), by the oxygen oxidation of butyraldehyde (391, 392), by the electrochemical oxidation of butyl alcohol (440), by the oxygen oxidation of butyric acid in the presence of filtered or unfiltered ultraviolet radiation (165), and by the reaction of boric–butyric anhydride with hydrogen peroxide (184).

Perbutyric acid is similar to the other peracids discussed, except that it is more stable and it deflagrates with less force than perpropionic acid, with partial carbonization (184). The pure compound has not been reported, but the mixture containing 95.4 per cent perbutyric acid melts at −10.5°C. (184) and a product containing 71.8 per cent boils at 26–30°C. at 12 mm. (219). When heated at 150°C. in a steel bomb perbutyric acid explodes, yielding much methane, carbon dioxide, carbon monoxide, and carbon, and a little propylene (214).

5. Miscellaneous

The remaining aliphatic peracids described have been studied to a limited extent, and in most cases only their method of preparation has been reported.

Perisovaleric acid, b.p. 31–32°C. at 1 mm., and perheptanoic acid have been prepared by the reaction of the corresponding aldehydes in carbon tetrachloride solution with ozone–oxygen mixtures (219). Perisovaleric acid has also been

[5] See footnote 2.

prepared by treating isovaleric acid with oxygen in unfiltered ultraviolet radiation (165).

Percaproic acid (m.p. 15°C.; b.p. 61–62°C. at 13 mm. and 41–42°C. at 0.5 mm.) has been prepared by the reaction of caproic anhydride with 93 per cent hydrogen peroxide (216). It has also been prepared by the reaction of caproic acid with 30 per cent hydrogen peroxide (271). Percaproic acid is apparently formed as an intermediate in the electrolysis of caproic acid and potassium caproate, but under these conditions it decomposes to carbon dioxide and amyl alcohol (210, 216). Percaproic acid is readily soluble in ethyl alcohol, diethyl ether, and petroleum ether, and slightly soluble in water. It decomposes slowly on storage at room temperature, and on rapid heating it detonates and ignites. On heating in a metal pipe at 240°C. it yields 1-pentene, *n*-caproic acid, *n*-amyl caproate, and carbon dioxide. It displays typical peracid properties, rapidly liberating iodine from potassium iodide and imparting a yellow color to titanium sulfate solution, and it is rapidly decomposed by concentrated potassium hydroxide (216).

Percrotonic acid has been prepared in dilute aqueous solution by the mild hydrolysis of crotonyl peroxide (173). Solutions containing 50 per cent percrotonic acid have been prepared by the reaction of crotonic anhydride with 94 per cent hydrogen peroxide (215). Attempts to obtain the pure peracid by distillation have been unsuccessful because of its instability. On being heated rapidly in a steel bomb percrotonic acid explodes, yielding carbon dioxide, unsaturated hydrocarbons, crotonic acid, and resins (215).

D'Ans and Frey (184) have reported that they detected perpalmitic acid, but no details were given. They presumably prepared this peracid by the reaction of palmitic acid with concentrated hydrogen peroxide.

Pertrichloroacetic acid has been prepared by the reaction of trichloroacetic anhydride with pure hydrogen peroxide (211), but the peracid is extremely unstable, being rapidly converted to phosgene, hydrogen chloride, carbon dioxide, and chlorine. Permonochloroacetic acid has been similarly prepared and can be distilled. It boils at 33–34°C. at 3.5–4 mm. (182, 398). Permonochloropropionic, perdichloropropionic, perbromopropionic, permonochloroacetic, perdichloroacetic, and perbromoacetic acids have been mentioned in a patent but no preparative details were given (268).

Perlactic, perglycolic, perpyruvic, and permesoxalic acids have been reported as intermediates in the oxidation of the corresponding aliphatic acids with hydrogen peroxide (238, 241, 245). Perlauric acid has been mentioned in a recent paper (485) but a description of its preparation or properties was not reported.

Long-chain persulfonates of unknown structure have been prepared by treating stearic acid with chlorosulfonic acid, followed by reaction of the resulting sulfonyl chloride with sodium peroxide (192, 336).

Hatcher and Holden (239, 241) have reported that peroxalic acid is not formed when oxalic acid is treated with dilute aqueous hydrogen peroxide. Koch and Maisin (301), however, have indicated that this peracid can be obtained from oxalic acid and hydrogen peroxide by the procedure of D'Ans and Kneip (189),

but no details were given. Milas and Panagiotakos (362) prepared diperoxalic acid by treating a pyridine–ether solution of hydrogen peroxide with oxalyl chloride at −20°C. This peracid is reported to be a powerful oxidizing agent, but no additional information regarding its properties could be found.

Monopersuccinic acid, m.p. 107°C. (with decomposition), has been prepared by the mild aqueous hydrolysis of β-carboxypropionylperoxide (172). It is purified by crystallization from a mixture of chloroform and ether. It is more soluble in water than is succinic acid, and it is also soluble in alcohol, acetone, and ethyl acetate. This peracid is relatively stable, and on being heated it liberates approximately 1 mole of carbon dioxide per mole of peracid (172). Dilute aqueous solutions of this peracid have been obtained by treating succinic anhydride with dilute aqueous solutions of hydrogen peroxide or persalts, such as sodium peroxide or sodium perborate (448, 449, 450, 452).

The preparation of dilute solutions of other aliphatic peracids, such as permaleic, perglycolic, and perglutaric acids, by the reaction of the corresponding acid anhydride with a dilute solution of an inorganic peroxide, has been mentioned in several patents (448, 449, 450, 452).

Tertiary butyl peresters of stearic, undecylenic, crotonic, succinic, and adipic acids have been prepared in good yields by treating tertiary butyl hydroperoxide with the appropriate acid chloride (363) but, as discussed earlier, these products are properly classified as derivatives of tertiary butyl hydroperoxide and organic acids rather than as derivatives of organic peracids.

B. AROMATIC AND CYCLIC PERACIDS

1. Perbenzoic acid

Perbenzoic acid was apparently isolated for the first time by Baeyer and Villiger (30, 31), who treated benzoyl peroxide with sodium ethoxide in ether–alcohol solution, followed by acidification. Subsequent investigators have had difficulty in obtaining good yields by their technique, however, and numerous modifications and improvements have been introduced. Levy and Lagrave (317) and Tiffeneau (513) carried out the reaction in toluene solution and reported 80–93 per cent yields. Hibbert and Burt (258), who studied the numerous experimental variables involved, pointed out that the order of addition of the reactants is important. They obtained 90 per cent yields. Braun (138) employed methyl alcohol–chloroform mixture as the solvent and sodium methoxide as the base and reported 82–86 per cent yields. Kleinschmidt and Cope (299a) employed methylene chloride instead of chloroform to extract the perbenzoic acid, and Harris and Smith (237) employed ligroin. Brooks and Brooks (153) and Bergmann and Witte (55) treated benzoyl chloride with aqueous sodium peroxide at low temperatures and reported yields of perbenzoic acid of 91 and 80 per cent, respectively. Wieland and coworkers (564) employed benzene–ethyl alcohol mixtures and reported 80–90 per cent yields. Isii (271) treated benzoic acid with hydrogen peroxide and reported the formation of perbenzoic acid, but he did not give details and yields. Calderwood and Lane (161) employed carefully washed chloroform and an excess of sulfuric acid. Rochen (462) employed benzoyl peroxide and

aqueous sodium peroxide or alcoholic sodium hydroxide, and obtained 50–55 per cent and 60–90 per cent yields, respectively. Kolthoff, Lee, and Mairs (303) reported that Braun's procedure (138) was the best for preparing perbenzoic acid but introduced the following modifications: (*a*) The reaction mixture was maintained below 0°C. during the addition of the chloroform solution of benzoyl peroxide, (*b*) the solution was extracted immediately after the addition was complete, (*c*) water was added before transferring the solutions to the separatory funnel, (*d*) carbon tetrachloride was used for washing instead of chloroform, (*e*) any emulsion was discarded, (*f*) after acidification, benzene rather than chloroform was employed for extraction, and (*g*) the benzene solution was stored in the dark at about 10°C.

Perbenzoic acid can also be prepared by the oxygen oxidation of benzaldehyde under controlled conditions. The oxygen oxidation of benzaldehyde to yield benzoic acid has been studied since the early part of the nineteenth century (579), but only comparatively recent investigators (31, 80, 221, 350, 563) have suggested that perbenzoic acid is an intermediate in this reaction, although the peracid was not isolated. Jorissen and van der Beek (279, 280, 281, 542), however, were apparently the first workers to isolate perbenzoic acid from such a system. They treated benzaldehyde, dissolved in a series of solvents, with oxygen while exposing the solutions to sunlight, and they reported that, in acetone solution, they obtained a 63 per cent yield of percompound. On evaporation of the solvent and vacuum distillation of the residue, perbenzoic acid was isolated. Acetone was by far the best solvent and carbon tetrachloride was moderately satisfactory. Jorissen and van der Beek prepared relatively small quantities of perbenzoic acid by this technique. Swern, Findley, and Scanlan (508) re-investigated this reaction and demonstrated that the reaction can be considerably accelerated by employing ultraviolet radiation instead of sunlight, and they prepared perbenzoic acid in 40 per cent yields on a fairly large laboratory scale. *p*-Bromobenzaldehyde, *p*-chlorobenzaldehyde, and *m*-chlorobenzaldehyde, however, yield little or no peracid when similarly treated (543).

The mechanism and kinetics of the reaction of oxygen with benzaldehyde, as well as conditions for accelerating and inhibiting the oxidation, have been studied by numerous workers (3, 26, 27, 28, 29, 77, 134, 155, 177a, 177b, 278, 281, 310, 349, 367, 444, 445, 446, 447, 455, 511, 531, 561, 562, 570, 571, 575, 576, 577, 578). Of interest is the observation of Wieland (561, 562, 571) that benzaldehyde autoxidizes at the same rate in the presence or absence of water, yielding perbenzoic acid, whereas in the autoxidation of acetaldehyde water must be excluded in order to obtain peracetic acid. Several investigators have pointed out that rigorously purified benzaldehyde does not autoxidize in the dark (310, 444, 445) and that the oxidation is retarded by infrared radiation (531). Some important inhibitors of this oxidation are iodine, hydroquinone, diphenylamine, and sulfur (367), pumice stone, Florida earth, and blood charcoal (155), lead tetraethyl, anthracene, phenol, and trichloroacetic acid (26), hydrocyanic acid and pyrophosphoric acid (310), catechol and resorcinol (77), and sulfur (278). The reaction is accelerated by sunlight (279, 280, 542), ultraviolet radiation (27, 444, 447, 508,

531), numerous metallic salts, notably those of manganese, iron, copper, silver, and nickel (310, 444, 446), and iron powder (542).

Perbenzoic acid can also be prepared by the reaction of benzaldehyde with ozone–oxygen mixtures (140, 141, 142, 144, 146, 147, 148, 149, 150, 219), by the reaction of benzoic acid with ozone (142), by the mild aqueous hydrolysis of benzoyl acetyl peroxide (173, 221), by the reaction of benzoyl acetyl peroxide with sodium ethylate (221), and by the reaction of benzoic anhydride with alkaline aqueous solutions of persalts or hydrogen peroxide (173, 448, 449, 450, 452).

Tertiary butyl perbenzoate (363) and *trans*-9-decalyl perbenzoate (178) have been prepared by the reaction of benzoyl chloride with tertiary butyl hydroperoxide and *trans*-9-decalin hydroperoxide, respectively.

Perbenzoic acid is a white crystalline solid, which can be crystallized from chloroform–ethanol mixtures (335) or from petroleum ether (31). It melts at about 41°C. (31, 219), and may be distilled under vacuum with partial decomposition. A boiling range of 97–110°C. at 13–15 mm. pressure has been reported (31). It is soluble in most common organic solvents, and slightly soluble in water. It may be sublimed, and it is somewhat volatile with steam. It has a strong, unpleasant odor, similar to that of hypochlorous acid.

Perbenzoic acid displays typical peracid oxidizing properties, liberating iodine rapidly from potassium iodide, decolorizing indigo, and oxidizing ferrous and manganese salts. The sodium, potassium, ammonium, and barium salts have been prepared and studied by Baeyer and Villiger (31). Other salts, such as the calcium, silver, and strontium salts, are too unstable to be isolated and purified (31). The barium salt, which is only slightly soluble in water, has been employed in the purification of perbenzoic acid (31). Perbenzoic acid yields benzoyl peroxide when treated with benzoyl chloride, and benzoyl acetyl peroxide when treated with acetic anhydride (31).

Perbenzoic acid is stable at room temperature, but it decomposes smoothly into benzoic acid, with the evolution of gases containing oxygen, when it is heated at 80–100°C. (31). It does not explode when struck but when heated in a steel bomb it detonates, yielding benzoic acid, oxygen, and traces of carbon dioxide (206). It has been reported to be stable in the presence of manganese dioxide, platinum, or silver (31), but recently Berezovskaya and Semikhatova (47) reported that the first two compounds catalyze its decomposition.

The stability of perbenzoic acid and of its sodium salt has been studied by many investigators (47, 89, 153, 161, 227, 303, 349, 357, 429, 511). Prileschajew (429) studied the kinetics of the decomposition of perbenzoic acid in chloroform, ether, and carbon tetrachloride solution. Böeseken and Blumberger (89) reported that perbenzoic acid is stable in chloroform above 30°C. Gelarie and Greenbaum (227) reported that at room temperature aqueous solutions of sodium perbenzoate evolve oxygen rapidly, yielding sodium benzoate in solution. The decomposition is accelerated by impurities, but even the pure compound in water is 95 per cent decomposed in 24 hr. Brooks and Brooks (153), however, showed that at 0°C. sodium perbenzoate is stable in the presence or absence of excess alkali. Meyer (349) reported that perbenzoic acid is stable at 0°C. in chloroform solution con-

taining benzaldehyde or acetate hemin but less stable when both benzaldehyde and alkali are present. He also showed that the peracid rapidly disappears in the presence of acids, phosphates, pyridine, or pyridine hemin. Berezovskaya and Semikhatova (47) demonstrated that the decomposition of perbenzoic acid in diethyl ether solution is catalyzed by platinum and that the presence of ethyl alcohol in the ether solution inhibits the reaction. Calderwood and Lane (161) showed that perbenzoic acid in unwashed chloroform at 6°C. begins to decompose within 1 to 2 weeks, whereas solutions in washed chloroform are perfectly stable for about two months. Kolthoff, Lee, and Mairs (303), however, have recommended that the use of chloroform as a solvent for perbenzoic acid be discouraged, since the peracid catalyzes the decomposition of the solvent by oxygen. Chloroform containing about 10 per cent of benzene is satisfactory.

Aqueous solutions of perbenzoic acid are reported to be germicidal (221). Perbenzoic acid can be employed for the vulcanization of rubber (396).

2. Miscellaneous

Monoperphthalic acid was first reported by Baeyer and Villiger (33), who prepared this compound by treating finely divided phthalic anhydride with an alkaline solution of dilute aqueous hydrogen peroxide, followed by acidification. Yields were not reported. They also prepared this peracid by hydrolyzing phthalyl peroxide with the calculated quantity of ice-cold sodium hydroxide solution, but no details of this method were given (33). The former reaction has been reinvestigated by Böhme (122, 123), who employed 30 per cent hydrogen peroxide and reported 65–70 per cent yields of monoperphthalic acid. Monoperphthalic acid has also been prepared by the reaction of phthalic anhydride with aqueous sodium perborate (448, 449, 450, 452, 495) and also with aqueous sodium peroxide (448, 449, 450, 452). Bachmann and Cooper (25) have reported that it is advantageous to employ 40 per cent sodium hydroxide and to add crushed ice to the reaction mixture when Böhme's method is employed.

Monoperphthalic acid is a white crystalline solid which softens at 110°C. and is converted to phthalic acid, with the evolution of gas (33). It is soluble in water and diethyl ether, and only slightly soluble in chloroform and benzene. It shows typical peracid oxidizing properties and is converted to hydrogen peroxide and phthalic acid on aqueous hydrolysis (33, 173).

Monoperphthalic acid is more stable than perbenzoic acid (33, 167), solutions of the former losing less than 10 per cent of their active oxygen content in 30 days at 0°C. and about 20 per cent at 12–14°C. (33). When chloroform is employed as a solvent, it should be freshly distilled before use (167).

In common with other organic peracids, monoperphthalic acid is reported to have a germicidal effect (221).

Tertiary butyl diperphthalate has been prepared by the reaction of phthalyl chloride with tertiary butyl hydroperoxide (363).

Diperterephthalic acid was also prepared by Baeyer and Villiger (33) by the reaction of terephthalyl chloride in ether solution with an alkaline solution of hydrogen peroxide. The free acid is a white crystalline solid, slightly soluble

in water, which explodes when heated or struck. It is readily converted to terephthalic acid by reducing agents and it is similar to perbenzoic acid in reactivity.

Dimethyl, diethyl, dipropyl, and diisopropyl perterephthalates have been prepared from terephthalyl chloride and the barium salt of the corresponding hydroperoxides (32, 343, 458).

Percinnamic acid has been prepared in 80 per cent yield by Bodendorf (76) by the reaction of cinnamyl peroxide with sodium ethylate in ethyl alcohol–chloroform solution. It melts at 67–68°C. (with decomposition), and it is relatively stable. In benzene solution at room temperature it remains unchanged for days, and when the solution is maintained at 50°C. for 24 hr., only 12 per cent of the active oxygen is lost.

p-Methoxyperbenzoic, *p*- and *m*-nitroperbenzoic, α- and β-pernaphthoic, and phenylperacetic acids have been prepared from the corresponding diacyl peroxide and sodium ethylate (345).

Although Baeyer and Villeger (33) stated that Brodie (152) may have obtained the barium salt of percamphoric acid in 1864, the free acid was first isolated and characterized by Milas and McAlevy (359), who treated *d*-camphoric anhydride with an aqueous solution of sodium peroxide. The peracid is a white solid which melts at 49–50°C., and is soluble in water and nearly all organic solvents. It is hydrolyzed in aqueous solution to camphoric acid and hydrogen peroxide. Percamphoric acid is more stable than perbenzoic acid (357). It is stable for weeks at 0°C. in the absence of moisture, and at room temperature it decomposes slowly to camphoric acid and oxygen. When heated at 80–100°C. it decomposes explosively.

The secondary methyl perester tertiary methyl camphorate has been prepared by the reaction of the barium salt of methyl hydroperoxide with tertiary methyl ester secondary camphoryl chloride (359).

Perfuroic acid has been prepared by Milas and McAlevy (360) by the reaction of difuroyl peroxide with sodium methoxide in diethyl ether–methyl alcohol solution. This peracid is probably obtained in small quantity during the autoxidation of furfural at 0°C. in petroleum ether, but it is not isolable from such a system (360). The preparation of dilute solutions of this peracid by the reaction of furoic anhydride with alkaline solutions of inorganic peroxides has been described in patents (448, 449, 450, 452). Perfuroic acid is a crystalline compound, melting at 59.5°C. (with decomposition), which can be recrystallized from carbon tetrachloride. Perfuroic acid is extremely soluble in water, and on standing hydrolyzes to furoic acid and hydrogen peroxide. It is insoluble in petroleum ether and soluble in most of the other common organic solvents. At 0°C. in chloroform solution, as well as in the absence of solvent, perfuroic acid is fairly stable, but at 30–40°C. it decomposes with explosive violence, yielding furoic acid, carbon dioxide, an alkali-soluble resin, and small amounts of 4,5-epoxyfuroic acid (361). At room temperature, decomposition of the peracid ranging from moderate to violent explosions may be caused by the addition of small quantities of organic and inorganic solids, such as animal charcoal and barium, calcium, strontium,

copper, and magnesium chlorides (361). Exposure of the solid acid or its acetic acid solution to ultraviolet light of wave lengths ranging from 4500 to 3600 Å. causes rapid decomposition. In chloroform solution at 35° and 40°C., the decomposition is monomolecular (361).

Tertiary butyl perfuroate has been prepared by the reaction of furoyl chloride with tertiary butyl hydroperoxide (363).

Several aromatic sulfur-containing peracids have been reported. Willstätter and Hauenstein (573) prepared a solution of benzoyl monopersulfuric acid by the reaction of monopersulfuric acid with benzoyl chloride at 0°C. The free acid cannot be isolated but the potassium salt, melting at 50–55°C., can be. The salt is soluble in water and detonates when ground or when heated at 70–80°C. When shaken with sulfuric acid, it is cleaved to perbenzoic and sulfuric acids, whereas on treatment with aqueous alkali it is converted to benzoic and monopersulfuric acids. Salts of *p*-toluenepersulfonic, *β*-naphthalenepersulfonic, and amylnaphthalenepersulfonic acids have been prepared from sodium, calcium, or silver peroxide and the corresponding arylsulfonyl chlorides (192, 336). Other related persulfonic acids have been prepared by the reaction of peroxides of the types $RSO_2O_2SO_2R$ and $RSO_2O_2SO_2R'$ with peroxides (336), and also by the reaction of metallic salts of organic sulfonic acids with hydrogen peroxide and aqueous sodium peroxide (336). A complex persulfuric acid has been prepared by treating *o*-phenanthrolene with silver salts and ammonium persulfate (336).

III. Organic Peracids as Oxidizing Agents

A. Oxidation of unsaturated compounds

1. Preparation of oxirane (α-epoxy) compounds

The preparation of oxirane compounds by the reaction of unsaturated substances with an organic peracid was discovered by the Russian chemist Prileschajew (425, 428, 429, 430, 431), who demonstrated that perbenzoic acid is an efficient oxidizing agent for this reaction and that the reaction is a general one for the epoxidation of compounds with isolated double bonds. The reaction proceeds as shown in equation 2.

$$-\overset{|}{C}=\overset{|}{C}- + C_6H_5CO_3H \xrightarrow[\text{solvents}]{\text{organic}} -\overset{|}{C}\!\!-\!\!\overset{|}{C}- + C_6H_5CO_2H \qquad (2)$$

(with O bridging the two carbons)

Although considerable evidence has been collected that the reaction proceeds as shown in the equation, some workers (376, 511) have suggested that the peracid adds directly to the double bond, followed by splitting out of benzoic acid. This erroneous idea has found its way into a standard reference work on organic chemistry (2).

This epoxidation reaction, which is an excellent one for preparative purposes, proceeds under mild reaction conditions and is conducted in a convenient organic solvent, such as chloroform, ether, acetone, and dioxane. The reaction time varies considerably and depends to a great extent on the number and nature of the groups attached to the unsaturated linkage (501) (discussed in greater detail in

Section V). In many of the epoxidations, quantitative yields of oxirane compounds are obtained, yields above 75 per cent usually being obtained. The reaction is especially valuable for the epoxidation of non-volatile, water-insoluble, unsaturated compounds, which usually cannot be satisfactorily converted to the oxirane compound either by way of the chlorohydrin or by direct oxidation with oxygen. Epoxidation with perbenzoic acid has been used in the preparation of oxirane compounds from a large number of unsaturated substances, which are listed alphabetically in table 1.

Since perbenzoic acid can be conveniently and readily prepared by the oxygen oxidation of benzaldehyde (279, 280, 281, 508, 542), several groups of investigators have treated solutions of benzaldehyde and an unsaturated compound with air or oxygen. The perbenzoic acid is consumed as it is formed. This application of the perbenzoic acid epoxidation technique, in which the isolation of the peracid is avoided, has been applied to the oxidation of octenes (407), oleic acid (447, 508), stilbene (447), styrene (447) and squalene (447); in general, good yields of oxirane compounds are obtained.

Monoperphthalic acid has also been employed to convert unsaturated compounds to the corresponding oxirane compounds, but this reaction has not been studied so extensively as epoxidation with perbenzoic acid. Although Böhme (122, 124) was apparently the first to demonstrate that monoperphthalic acid is consumed by reaction with double bonds, Chakravorty and Levin (167) were the first investigators actually to isolate oxirane compounds by the oxidation of unsaturated compounds with this oxidizing agent. The epoxidation reaction is conducted under the same conditions as that with perbenzoic acid, and good yields of oxirane compounds are usually obtained. Epoxidation with monoperphthalic acid has been applied most extensively to naturally occurring products such as sterols and polyenes. Unsaturated substances which have been converted to oxirane compounds by oxidation with monoperphthalic acid are listed alphabetically in table 2.

For a long time it was assumed that oxirane compounds could not be prepared by the epoxidation of olefins with peracetic acid, since the products usually isolated from such reactions were α-glycols or hydroxyacetates (see later discussion). Böeseken, Smit, and Gaster (111) and Smit (486), however, obtained methyl 9,10,12,13-diepoxystearate by the epoxidation of methyl linoleate with peracetic acid in acetic acid solution, but yields were not reported. When this work was repeated in our laboratory (503), we found that the yield of product is extremely low, the major proportion of the methyl linoleate being converted to a polymer of unknown constitution. Subsequent investigators have reported that oxirane compounds can be obtained from a few unsaturated compounds by oxidation with peracetic acid in acetic acid solution, but yields have either not been reported or are low (30 per cent or less). Compounds epoxidized in this manner were 3,6-diacetoxy-5-methylnorcholestane (405), dihydrocaryophyllene (386), elaidic acid and methyl elaidate (297), ergosterol maleic-anhydride adduct (261), 5-methylnorcholestane-3,6-dione (405), β-amyrin acetate (492), and *trans*-7-octadecenoic acid (410).

In an important investigation, however, Arbuzow and Michailow (22) treated

TABLE 1

Unsaturated substances converted to oxirane α-epoxy compounds by oxidation with perbenzoic acid

SUBSTANCE	REFERENCES
3(β)-Acetoxy-20-oxo-5-allo-Δ^{16}-pregnene	(414)
Acetyllinaloöl	(431)
20-Allopregnene-3(β),17(β)-diol 3-monoacetate	(476b)
20-Allopregnene-3(β),17(β)-diol diacetate	(476b)
Allyl alcohol	(425, 430)
d-α-Amyrilene	(473)
β-Amyrilene	(473, 474)
β-Amyrin	(473, 474)
5-Androstene-3,17-dione	(465)
9-Androstene-3,17-dione	(412)
9-Androstene-3(β)-ol-17-one acetate	(453)
β-Anhydrodigoxigenin diacetate	(416)
β-Anhydrodihydrodigoxigenin diacetate	(416)
Anhydro-[4-(enol)acetobutyl alcohol]	(49, 51)
1-Anisyl-2,2-diphenylethylene	(311, 556)
1-Anisyl-1-(*m*-methoxyphenyl)ethylene	(321)
1-Anisyl-1-(*o*-methoxyphenyl)ethylene	(321)
Apocholenic acid	(566)
Apocholic acid	(126, 162, **567**)
Benzaldehyde phenylhydrazone	(54)
1-Benzyl-1-cyclohexene	(369)
1-Benzyl-2,2-diphenylethylene	(311)
Benzylethylene	(323, 325)
Benzylideneacetone	(431)
1-(2-Biphenylyl)-1-phenyl-2,2-diethylethylene	(133)
Brassidic acid	(196)
p-Bromobenzylethylene	(439)
4-(*p*-Bromophenyl)-1-butene	(439)
Butadiene	(438)
1-Butyl-1-cyclohexene	(369)
1-Butyl-2,2-diphenylethylene	(311)
1-Isobutyl-2,2-diphenylethylene	(311)
$C_{15}H_{24}$ (two C=C)	(313)
Camphene	(208)
Caprylene	(425, 428)
d-3-Carene	(22)
Carotene	(207)
Caryophyllene	(476, 536)
1-Chloro-1-cyclohexene	(369, 373)
1-Chloro-2-cyclohexene	(371, 373)
1-Chloro-1-cyclopentene	(373)
1-Chloro-2-cyclopentene	(373)
1-Chloro-1-heptene	(426)
2-Chloro-1-methyl-1-cyclohexene	(373)
3-Chloro-1-methyl-3-cyclohexene	(371, 373)
1-Chloromethyl-2-phenylethylene	(220)
2-Chloro-1-methylenecyclohexane	(374)
2-Chloro-2-octene	(426)

TABLE 1—*Continued*

SUBSTANCE	REFERENCES
4-Cholestene	(247, 413)
5-Cholestene	(413, 467)
Δ^5-Cholesten-3-one	(465)
γ-Cholestenyl acetate	(159a)
Cholesterol	(413, 465, 559)
Cholesteryl acetate	(465)
Cholesteryl benzoate	(261, 493)
Cholesteryl chloride	(247)
Cinnamyl acetate	(273)
Cinnamyl alcohol	(273)
Citral	(425, 431)
Citronellal	(425, 430)
Citronellol	(308a)
Copaene	(139a)
Crotonic acid	(136)
Crotyl alcohol	(273)
Cycloheptene	(94)
1,3-Cyclohexadiene	(43)
Cyclohexene	(85, 308)
Cyclopentene	(85)
1-Decene	(464)
Decene	(425)
Dehydroandrosterone	(538, 539)
3-*trans*-Dehydroandrosterone	(351)
trans-Dehydroandrosterone acetate	(469)
Dehydroergosteryl acetate–maleic anhydride adduct	(261)
Dehydroisoandrosterone	(201)
Dehydroisoandrosterone acetate	(200)
3,6-Diacetoxy-5-methylnorcholestane	(405)
3(β),21-Diacetoxy-20-oxo-5-allo-$\Delta^{14,16}$-pregnadiene	(415)
3,4-Diacetoxystyrene	(281a)
Diallyl	(84)
1,1-Dibenzyl-2-anisylethylene	(521)
1,1-Dicyclohexylethylene	(547)
Dicyclopentadiene	(38, 564)
1,1-Diethoxy-2-butene	(220)
1,1-Diethyl-2-anisylethylene	(521)
1,1-Diethyl-2-phenylethylene	(326)
Dihydro-β-amyrilene	(474)
Dihydrocaryophyllene	(476)
Dihydrocyclopentadiene	(564)
1,2-Dihydronaphthalene	(512)
2,3-Dihydronaphthalene	(93)
1,4-Dihydronaphthalene	(93, 512)
5,6-Dihydro-1,2-pyran	(401)
3,7-Dihydroxycholenic acid	(565)
4,5-Dihydroxy-2,6-octadiene	(273)
2,3-Dihydroxy-1-propene (acetone compound)	(218)
Diisobutylene	(425, 429)
1,1-Dimethyl-2-anisylethylene	(515, 521, 522)

TABLE 1—*Continued*

SUBSTANCE	REFERENCES
2,3-Dimethyl-2-butene	(429)
Dimethylcyclohexene	(429)
1,2-Dimethylcyclohexene	(381)
1,3-Dimethyl-1-cyclohexene	(369)
2,4-Dimethyl-1-cyclohexene	(369)
1,1-Dimethyl-2,2-diphenylethylene	(441)
1,2-Dimethyl-1,2-diphenylethylene	(441)
1,1-Dimethyl-2-(*m*-methoxyphenyl)ethylene	(320)
1,1-Dimethyl-2-(*o*-methoxyphenyl)ethylene	(320)
1,1-Dimethyl-2-methyl-2-phenylethylene	(334)
1,1-Dimethyl-2-phenylethylene	(326, 515, 522)
1,1-Dimethyl-2-piperonylethylene	(516, 520)
1,1-Dimethyl-2-tolylethylene	(516, 519)
2,4-Dimethyl-4-vinyl-1-cyclohexene	(313)
1,1-Dipropyl-2-anisylethylene	(521)
1,1-Di-*p*-tolylethylene	(442)
1-Dodecene	(40, 464)
Elaidic acid	(24, 38, 88, 502)
3,9-Epoxy-Δ^{11}-cholenic acid	(340)
Erucic acid	(38, 196)
1-Ethoxy-2-cyclohexene	(370)
Ethyl acetoacetate	(101)
1-Ethyl-2-anisylethylene	(316)
1-Ethyl-1-benzyl-2-phenylethylene	(326)
1-Ethyl-2-(*p*-bromophenyl)ethylene	(439)
Ethyl cinnamyl ether	(190)
1-Ethyl-2,2-dianisylethylene	(555)
1-Ethyl-2,2-diphenylethylene	(311, 319, 555)
Ethyl elaidate	(88)
1-Ethyl-1-ethoxy-2,2-dipropylethylene	(36)
Ethyl hendecenoate (undecylenate)	(327)
Ethyl 9,12,15-octadecatrienoate (linolenate)	(39)
Ethyl oleate	(37, 38, 39, 88)
1-Ethyl-2-phenyl-2-anisylethylene	(555)
1-Ethyl-2-phenylethylene	(316)
1-Ethyl-2-propyl-2-anisylethylene	(554)
Ethyl vinyl ether	(50)
11-Etiocholen-3(α)-ol-17-one acetate	(311a)
Δ^9-Etiocholen-3(α)-ol-17-one	(194)
Furfural diacetate	(484)
Furfural phenylhydrazone	(54)
Geraniol	(308a, 425, 428, 431)
Glucal	(52, 53)
1-Hendecene	(464)
Hendecenoic (undecylenic) acid	(237)
1-Heptene	(322)
1-Isoheptene	(322)
3-Heptene	(209)

TABLE 1—*Continued*

SUBSTANCE	REFERENCES
3(α)-Hydroxy-$\Delta^{9,11}$-cholenic acid	(340)
3(α)-Hydroxy-Δ^{11}-cholenic acid	(341)
11-Hydroxy-11,11-diphenyl-1-hendecene	(327)
11-Hydroxy-1-tetradecene	(327)
11-Hydroxy-1-tridecene	(327)
Indene	(38, 85, 93, 369)
α-Ionone	(387)
β-Ionone	(387)
Isodihydroxycholenic acid	(568)
Isoprene	(438, 456)
Isosafrole	(516)
Isostilbene	(295)
11-Keto-11-phenyl-1-hendecene	(327)
11-Keto-1-tetradecene	(327)
11-Keto-1-tridecene	(327)
Lanostenone	(44)
Lanosteryl acetate	(44, 197)
Limonene	(23, 346, 425, 428)
Linaloöl	(385, 425, 431)
Linolenic acid	(37, 39)
3-*p*-Menthene	(511)
1-Menthen-6-ol	(433)
Methyl $\Delta^{14,16}$-3(β)-acetoxyalloetiocholadienate	(472a)
Methyl 3(α)-acetoxy-$\Delta^{9,11}$-cholenate	(261, 484a)
Methyl 3(α)-acetoxy-Δ^{11}-cholenate	(420)
Methyl 3(β)-acetoxy-Δ^{11}-cholenate	(420)
Methyl 3(α)-acetoxy-12(α)-hydroxy-Δ^{7}-cholenate	(56b)
1-Methyl-2-anisylethylene	(316)
1-Methyl-1-benzyl-2-phenylethylene	(326)
Methyl brassidate	(196)
1-Methyl-2-(*p*-bromophenyl)ethylene	(439)
Methyl Δ^{9}-cholenate	(454)
Methyl Δ^{11}-cholenate	(4)
Methyl cinnamyl ether	(190, 273)
3-Methylcyclohexanone (enol acetate)	(372)
1-Methyl-1-cyclohexene	(85, 308, 335, 383)
4-Methyl-1-cyclohexene	(369, 379)
5-Methyl-1-cyclohexene	(308)
6-Methyl-1-cyclohexene	(308)
1-Methyl-1-cyclopentene	(85, 335)
d-3-Methyl-1-cyclopentene	(369)
4-Methyl-1-cyclopentene	(369)
Methyl diacetylapocholate	(568)
Methyl 3(α),12(β)-diacetylapocholate	(417)
Methyl Δ^{14}-3(α),12(β)-diacetoxycholenate	(417)
Methyl $\Delta^{7,14}$-3(α),12(β)-diacetoxycholadienate	(417)
1-Methyl-2,2-dianisylethylene	(555)
Methyl *d*-dihydropimarate	(466)
Methyl 3,7-dihydroxycholenate	(126)

TABLE 1—*Continued*

SUBSTANCE	REFERENCES
1-Methyl-2,2-diphenylethylene	(311, 319, 555)
1-Methyl-1,2-diphenylethylene	(517)
Methyl elaidate	(38)
Methylenecyclohexane	(523)
2-Methylenedecahydronaphthalene	(369)
Methyl erucate	(196)
1-Methyl-1-ethyl-2-anisylethylene	(554)
1-Methyl-2-ethyl-2-anisylethylene	(554)
4-Methyl-2-ethylcyclohexene	(369)
3-Methyl-1-ethylidenecyclohexane	(368, 369)
1-Methyl-1-ethyl-2-phenylethylene	(326)
Methyl hendecenoate (undecylenate)	(327)
Methyl heptenone	(430)
Methyl 2,4-hexadienoate (sorbate)	(248, 250)
Methyl 3(α)-hydroxy-Δ^{11}-cholenate	(420)
Methyl 3(β)-hydroxy-Δ^{11}-cholenate	(420)
Methyl 3(α)-hydroxy-12-methoxy-$\Delta^{9,11}$-cholenate	(478)
Methyl 3-keto-Δ^{11}-cholenate	(157)
Methyl 3-keto-$\Delta^{4,11}$-choladienate	(157)
Methyl 12-methoxy-$\Delta^{9,11}$-cholenate	(478)
3-Methyl-1-methylenecyclohexane	(369)
3-Methyl-1-methylenecyclopentane	(369)
Methyl 9,11-octadecadienoate	(341, 486)
Methyl 9,12-octadecadienoate (linoleate)	(111, 231, 411, 486)
Methyl oleate	(508)
Methyl petroselaidate	(498)
Methyl petroselinate	(498)
1-Methyl-1-phenylethylene	(46a, 180)
1-Methyl-2-phenylethylene	(46a, 316, 519)
Methyl *d*-pimarate	(466)
4-Methyl-2-propyl-1-cyclohexene	(369)
1-Methyl-1-propyl-2-phenylethylene	(326)
Methyl ricinelaidate	(111, 486)
Methyl ricinoleate	(486)
Methyl styryl carbinol	(375)
1-Nonene	(464)
9-Octadecene	(88)
Octenes	(407)
Oleic acid	(37, 38, 39, 88, 408, 447, 502, 508)
Oleyl alcohol	(504, 508)
1-Phenyl-2-anisylethylene	(515, 518)
1-Phenyl-2-benzylethylene	(316)
cis-Phenylbutadiene	(376)
4-Phenyl-1-butene	(323, 325)
1-Phenyl-1-cyclohexene	(85, 324, 335, 382)
1-Phenyl-1-cyclopentene	(85, 335)
1-Phenyl-2,2-dibenzylethylene	(515, 518)
6-Phenyl-1-hexene	(323, 325)
1-Phenyl-1-(*m*-methoxyphenyl)ethylene	(321)

TABLE 1—*Concluded*

SUBSTANCE	REFERENCES
1-Phenyl-1-(*o*-methoxyphenyl)ethylene	(321)
1-Phenyl-4-methylcyclohexene	(324)
5-Phenyl-1-pentene	(323, 325)
1-Phenyl-2-piperonylethylene	(516, 520)
1-Phenyl-2-(*p*-tolyl)ethylene	(516, 519, 556)
Pinene	(208, 384, 425, 428, 432)
5-Pregnen-20-one-3(β),21-diol 21-monoacetate	(200)
2-Propenyldioxolane	(220)
1-*n*-Propyl-2-anisylethylene	(316)
1-*n*-Propyl-1-benzyl-2-phenylethylene	(326)
1-Isopropyl-1-benzyl-2-phenylethylene	(326)
1-*n*-Propyl-1-cyclohexene	(369)
1-Isopropyl-1-cyclohexene	(369)
1-*n*-Propyl-1-cyclopentene	(369)
1-Isopropyl-1-cyclopentene	(369)
1-*n*-Propyl-2,2-diphenylethylene	(311)
1-Isopropyl-2,2-diphenylethylene	(311)
1-*n*-Propyl-2-phenylethylene	(316)
1-Isopropyl-2-phenylethylene	(316)
Pulegone	(427)
Rubber	(435, 436)
Squalene	(447)
Stilbene	(95, 295, 447, 515)
Styrene	(46a, 93, 258, 259 281a, 447)
1,2,3,4-Tetrahydronaphthalene	(308)
Tetraphenylethylene	(318)
Thiopyrine	(306)
1-Tridecene	(464)
1,2,5-Trimethyl-5-isopropenyl-1-cyclohexene	(313)
Triphenylethylene	(311, 556)

d-Δ^3-carene with a solution of peracetic acid in acetic acid solution and also with an ether solution of peracetic acid. With the first oxidizing solution they obtained hydroxyacetates, whereas with the second they obtained good yields of oxirane compound. Similarly, α-pinene is converted to the oxirane compound in 89 per cent yield by means of peracetic acid in ether solution. With peracetic acid in chloroform solution α-pinene, however, is converted to the oxirane compound in only fair yield, the major proportion of the product being converted to the hydroxyacetate. In a subsequent report (23), these investigators extended their work to other olefins, and demonstrated that limonene, cyclohexene, anethole, and isoeugenol can be converted to oxirane compounds in good yield by employing an ether solution of peracetic acid. They concluded, therefore, that the behavior of peracetic acid toward olefins is the same as that of perbenzoic acid—namely, it converts the double bond to the oxirane group—but when an acetic acid solution of peracetic acid is employed, the oxirane compound is converted to the hydroxyacetate by further reaction with the acetic acid.

Peracetic acid in an inert solvent has also been applied by Böeseken and Schneider (104) to the epoxidation of cyclohexene, stilbene, and isostilbene, by Pigulevskiĭ (407) to the epoxidation of octenes, and by Tanaka (511) to the epoxidation of stilbene and 3-*p*-menthene.

TABLE 2

Unsaturated substances converted to oxirane (α-epoxy) compounds by oxidation with monoperphthalic acid

SUBSTANCE	REFERENCES
3(β)-Acetoxy-20-oxo-5-allo-$\Delta^{14,16}$-pregnadiene	(414)
20-Allopregnene-3(β),17(β)-diol	(294a, 484a)
1-(2-Biphenylyl)-1-phenyl-2,2-dimethylethylene	(133)
Capsanthin diacetate	(287)
α-Carotene	(285)
β-Carotene	(284)
Cholesterol	(167)
Cholesteryl acetate	(167, 413)
Cholesteryl benzoate	(41, 167)
Cryptoxanthin diacetate	(288)
trans-Dehydroandrosterone acetate	(469, 471)
trans-Dehydroandrosterone benzoate	(469)
3(β),21-Diacetoxy-20-oxo-5-allo-$\Delta^{14,16}$-pregnadiene	(415)
α-Elemolic acid	(472b)
α-Ionone	(292)
β-Ionone	(292)
Linaloöl	(385)
2-Lupene	(274a)
Methyl Δ^{14}-3(β)-acetoxyalloetiocholenate	(416)
Methyl $\Delta^{14,16}$-3(β)-acetoxyetiocholadienate	(472)
Methyl Δ^{14}-3(β)-acetoxy-17-isoalloetiocholenate	(416)
Methyl α-elemolate	(472b)
Methyl α-ionone	(387)
Methyl *d*-pimarate	(475)
1-Phenyl-2-cyclohexylethylene	(514)
$\Delta^{14,17}$-Pregnadien-3-one	(468)
Rubixanthin	(290)
Vitamin A	(286, 289)
Xanthophyll diacetate	(283)
Zeaxanthin diacetate	(283)

The apparent necessity for employing peracetic acid in an inert solvent to obtain good yields of oxirane compounds from olefins was a serious drawback to the general applicability of peracetic acid for epoxidation, since peracetic acid can be prepared and used most conveniently in acetic acid solution, whereas its isolation free (or substantially free) of acetic acid is accomplished only with great difficulty. In connection with a kinetic study of the reaction of peracetic acid (approximately 1 molar) in acetic acid solution with various long-chain compounds having isolated, non-terminal double bonds, Findley, Swern, and Scanlan (217) observed that if the temperature is maintained between 20° and 25°C.

consumption of peracetic acid is substantially complete in 2–4 hr. when only 1.1–1.2 moles of peracetic acid per mole of double bond is employed, 85–95 per cent of the theoretical quantity of peracetic acid being consumed. The products isolated consisted of oxirane compounds containing only small amounts of hydroxyacetate and unreacted olefin. The reaction was shown to be a general one and afforded a simple and convenient method for the preparation of large quantities of oxirane compounds, and isolation of peracid and employment of inert solvents were unnecessary. This reaction was successfully applied (217) to the epoxidation of oleic acid, methyl oleate, elaidic acid, methyl hendecenoate (undecylenate), methyl ricinoleate, oleyl alcohol, triolein, lard oil, neatsfoot oil, olive oil, peanut oil, cottonseed oil, corn oil, soybean oil, tobaccoseed oil, menhaden oil, linseed oil, perilla oil, castor oil, and rapeseed oil. In a later investigation, Swern, Billen, and Scanlan (506) converted 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene to the corresponding oxirane compounds in fair yields by epoxidation with peracetic acid in acetic acid solution. The terminally unsaturated compounds require about 24 hr. reaction time, as compared with 2–4 hr. for olefins with non-terminal, isolated double bonds.

Comparison of the reaction conditions employed by Swern and coworkers (217, 506) with those employed by earlier investigators who studied the oxidizing action of peracetic acid in acetic acid solution on olefins reveals the reason for the failure of the earlier workers to obtain high yields of oxirane compounds. Swern and coworkers employed relatively short reaction periods and low temperatures, whereas the earlier investigators usually employed either long reaction periods at room temperature or short reaction periods at elevated temperatures, or the solution contained sulfuric acid (employed as the catalyst in the preparation of peracetic acid). Thus, Findley, Swern, and Scanlan (217) reported that certain long-chain oxirane compounds dissolved in a large excess of glacial acetic acid are converted to hydroxyacetates at the rate of about 1 per cent per hour at 25°C., but at 65°C. the conversion to hydroxyacetates is complete in only 4 hr., and at 100°C. it is complete in 1 hr. Furthermore, when peracetic acid solutions in glacial acetic acid containing 1 per cent of concentrated sulfuric acid are employed in epoxidation reactions, no oxirane compounds can be isolated and quantitative yields of hydroxyacetates are obtained, even when mild reaction conditions are employed (217, 506). The sulfuric acid catalyzes the ring-opening reaction of acetic acid with the oxirane group. Under the proper reaction conditions, however, peracetic acid in acetic acid solution can be employed as a general reagent for the epoxidation of the isolated double bond.

d-Pinene epoxide and cholesterol epoxide have also been prepared by the reaction of the corresponding unsaturated compounds with percamphoric acid (357).

2. Preparation of α-glycols

The utilization of peracetic acid for the preparation of α-glycols from unsaturated compounds far exceeds that of all other organic peracids combined. This peracid is usually employed in one of two ways. It is either preformed by the reaction of acetic acid or acetic anhydride with hydrogen peroxide, or the

unsaturated compound is mixed with hydrogen peroxide and acetic acid (with or without a sulfuric acid catalyst), and the peracetic acid is consumed as it is formed. In these reactions, the olefin is first converted to the oxirane compound, which can be isolated if no strong acid catalyst has been employed, if the reaction conditions are mild, and if the reaction is of sufficiently short duration (see earlier discussion). If the reaction mixture is heated at 65°C. for 4 hr. or 100°C. for 1 hr., the oxirane compound (in solution) is quantitatively converted to the hydroxyacetate, which in turn can be readily hydrolyzed to the α-glycol in quantitative yield. If the peracetic acid solution contains sulfuric acid, the oxirane compound is rapidly and quantitatively converted to the hydroxyacetate in a few hours even at 40°C. In many cases in which the oxirane compound has been isolated, it has also been converted to the α-glycol in excellent yield. Most investigators have effected this hydrolysis by means of concentrated alkali, although other techniques are preferable (502).

Although peracetic acid can be prepared by efficient processes, and only a small proportion 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. In an attempt to obviate the need for isolating peracetic acid, some workers have employed a solution of hydrogen peroxide in acetic acid to hydroxylate olefins. As employed by earlier workers, the reaction mixture or solution of 25–30 per cent hydrogen peroxide, acetic acid, and olefinic compound is allowed to stand at room temperature for long periods (262, 264), the reaction mixture is heated to accelerate peracid formation (262, 264), or the hydrogen peroxide and acetic acid are preheated to form peracetic acid, followed by addition of the compound to be hydroxylated without attempting to maintain the temperature below 40°C. (479, 480). By these procedures much active oxygen is lost, and although excellent yields of α-glycol can be obtained, a large excess of hydrogen peroxide must be employed. Recently, Swern and coworkers (505) demonstrated that by treating the olefin with 25–30 per cent hydrogen peroxide and acetic acid containing catalytic quantities of concentrated sulfuric acid, excellent yields of α-glycols can be obtained with the use of approximately stoichiometric quantities of hydrogen peroxide. Since the mineral acid catalyzes peracetic acid formation and since the peracid is rapidly consumed at 40°C., the reaction is complete in a few hours and little active oxygen is lost. This hydroxylation method is one of the most efficient for converting long-chain olefinic compounds to α-glycols. Recently, Greenspan (232) was able to achieve more complete hydroxylation with 90 per cent hydrogen peroxide instead of 25–30 per cent.

Numerous unsaturated substances have been hydroxylated by oxidation with peracetic acid, either preformed or by formation and utilization *in situ*. These substances are listed alphabetically in table 3. It is obvious that oxirane compounds prepared by the peracetic acid oxidation of olefins (already discussed) can be converted to α-glycols, and some earlier workers concerned primarily with the preparation of oxirane compounds have made the α-glycols from them. These unsaturated compounds are not listed in this table, since they have already been

TABLE 3

Unsaturated substances converted to α-glycols by oxidation with peracetic acid

SUBSTANCE	REFERENCES
Allostilbene	(95)
Allylacetic acid	(103)
Allylbenzene	(96)
Allylmalonic acids	(103)
Anethole	(96)
Benzyl 2-propenyl sulfone	(544)
Brassidic acid	(196)
Butadiene sulfone	(544)
2-Butene	(90)
d-Δ^1-Carene	(412)
d-Δ^3-Carene	(22)
Castor oil	(294, 480, 481, 482)
Cholesterol	(412a)
Cholesteryl acetate	(406)
Cocoa butter	(264)
Cyclohexene	(23, 96, 483)
3-*trans*-Dehydroandrosterone	(351)
3-*trans*-Dehydroandrosterone tetraacetylglucoside	(351)
Dehydroisoandrosterone acetate	(199)
Diisobutylene	(160, 260, 269)
Dimethylbutadiene sulfone	(544)
Isododecene	(269)
11,12-Eicosenoic acid	(267)
Elaidic acid	(24, 196, 262, 297, 394, 486, 502, 505)
Eleostearic acid	(99)
Eleostearic acid dibromide	(99)
Eleostearic acid tetrabromide	(99)
Erucic acid	(196, 463)
Ethyl elaidate	(486)
Ethyl eleostearate	(99)
Ethyl oleate	(479, 481, 482, 486)
Eugenol	(96)
Hendecenoic (undecylenic) acid	(103, 463)
Hendecenoic acid dimers	(463)
1-Heptene	(86)
3-Heptene	(86)
1-Hexadecene	(120, 235)
Indene	(96)
Isoprene	(86)
β-Isoprene sulfone	(544)
Isosafrole	(96)
Limonene	(509)
Linoleic acid	(231, 489)
3-Menthene	(483)
Methyl brassidate	(196)
1-Methyl-1-cyclohexene	(483)
3-Methyl-1,2-butadiene (dimethylallene)	(86)

TABLE 3—*Concluded*

SUBSTANCE	REFERENCES
Methyl elaidate	(262, 265)
Methyl erucate	(196)
2-Methyl-1-heptene	(86)
Methyl linoleate	(231)
Methyl oleate	(262, 265, 297)
Methyl palmitoleate	(262)
Methyl petroselinate	(263)
Isononene	(269)
Norbornylene	(70a)
9,11,13-Octadecatrienol (eleostearyl alcohol)	(491)
Oleic acid	(46, 196, 232, 262, 297, 394, 479, 481, 482, 486, 502, 505)
Oleyl alcohol	(479, 481, 482, 491)
Phenylbenzylethylene	(96)
Pregnenonol acetate	(199)
Ricinelaidic acid	(294)
Ricinoleic acid	(294)
Ricinoleyl alcohol	(491)
Safrole	(96)
Sorbic acid	(103)
Soybean oil	(270, 271, 272, 395)
Stilbene	(95)
Tallow	(264)

mentioned. Some of the unsaturated substances listed in table 3 have been converted to hydroxyacetates rather than to α-glycols, but the conversion of the acetate to the glycol is effected so readily that it was deemed desirable to include these substances.

Since the reaction of hydrogen peroxide with organic acids is an equilibrium reaction, the hydrogen peroxide will be completely consumed if the peracid reacts as it is formed. If reaction conditions favor rapid formation of the peracid without causing decomposition, stoichiometric utilization of the active oxygen should be feasible, since peracids react rapidly with many classes of oxidizable substances. With most aliphatic acids, however, formation of peracid is a relatively slow reaction at moderate temperatures. Thus, D'Ans and Frey (184) have shown that the reaction of approximately equimolar quantities of substantially anhydrous hydrogen peroxide and acetic, propionic, or butyric acid requires 12–16 hr. for attainment of equilibrium even when sulfuric acid is employed as catalyst. Unlike these aliphatic acids, however, formic acid reacts rapidly with hydrogen peroxide at moderate temperatures, yielding performic acid, and equilibrium is attained in less than 2 hr. with either 90–100 per cent hydrogen peroxide (184, 233) or even with 25–30 per cent hydrogen peroxide (507, 525). Swern and coworkers (505) have taken advantage of the unusual reactivity of formic acid and demonstrated that performic acid (507) or, preferably, 25–30 per cent hydrogen peroxide and formic acid (505), can be employed as an extremely efficient

hydroxylating reagent for the isolated double bond. These investigators obtained substantially quantitative conversion to the α-glycol in a short time, employing approximately stoichiometric quantities of hydrogen peroxide. The initial product of oxidation, however, is not the α-glycol but the oxirane compound, which is rapidly converted to hydroxyformates as a result of the high acidity of formic acid. The hydroxyformates are the products isolated and these are readily converted to the α-glycol by hydrolysis with dilute aqueous alkali or even by exposure to moist air or heating with water (502). This hydroxylation technique, which is probably the most efficient one known for long-chain unsaturated compounds with isolated double bonds, was applied by Swern and coworkers (505) to the oxidation of oleic acid, elaidic acid, oleyl alcohol, methyl ricinoleate and 10,11-hendecenoic (undecylenic) acid, and subsequently (506) to 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. Although solutions of performic acid can be separately prepared and then employed for hydroxylation purposes, its relative instability, as compared with peracetic acid and other aliphatic peracids (165, 189, 204, 233, 507, 525), causes appreciable quantities of active oxygen to be lost, and procedures in which previously prepared performic acid is employed are much less efficient, in general, than those in which performic acid is prepared and utilized *in situ*.

Recently, Greenspan (232) substituted 90 per cent hydrogen peroxide for the 25–30 per cent concentration and obtained slightly more complete reaction in the hydroxylation of oleic and 10,11-hendecenoic (undecylenic) acids. Also, English and Gregory (204) showed that concentrated performic acid can be used in the hydroxylation of α,β-unsaturated acids, giving the dihydroxy acids in fair yields, generally, within a relatively short time. Earlier workers, who had employed dilute peracids, had either been unable to hydroxylate such compounds or extremely long reaction times were required, with concomitant loss of active oxygen. α,β-Unsaturated compounds hydroxylated by English and Gregory (204) were 2-nonenoic, 2-hendecenoic, and cinnamic acids, and dimethyl traumatate and methyl 2-nonenoate. They also hydroxylated cyclohexene, obtaining good yields of *trans*-1,2-cyclohexanediol.

The early work of Isii (271) on the hydroxylation of soybean oil with performic acid, as well as with other organic peracids, is worthy of mention. No definite products were obtained, although he showed that the acetyl number of the treated soybean oil was higher than that of the original.

Recently, Weitkamp and coworkers (557) treated some monounsaturated acids obtained from human hair fat with hydrogen peroxide and formic acid and obtained the corresponding dihydroxy acids.

Although perbenzoic, monoperphthalic, and percamphoric acids are ordinarily not considered to be hydroxylating reagents, since the products usually obtained in the oxidation of olefins with these oxidants are the oxirane compounds, these peracids can be employed in the preparation of glycols, since the oxirane compound can be converted to the α-glycol in quantitative yield. In some cases this series of reactions has been carried out. In general, there is no advantage whatsoever in employing the aromatic peracids to prepare α-glycols when two more

efficient peracids are available for this purpose—namely, performic and peracetic acids, either preformed or prepared and used *in situ*. Under some reaction conditions, however, perbenzoic acid has converted the double bond either to the α-glycol group or to a benzoate ester readily hydrolyzable to the α-glycol, and oxirane compounds are not isolated. In these cases, water has been present or reaction times have been exceptionally long. Unsaturated substances which have

TABLE 4

Unsaturated substances converted to α-glycols by oxidation with perbenzoic acid

SUBSTANCE	REFERENCES
Anhydroacetobutyl alcohol	(49)
Apocholic acid	(162, 567)
Cellobial	(53)
2,4-Cholestadiene	(56)
Crotonic acid	(135)
Dihydroergosteryl acetate	(574)
1,1-Diphenylethylene	(390)
Elaidic acid	(394)
Ergosterol	(574)
α-Ergostenyl acetate	(574)
Furan	(117)
Galactal	(315)
Glucal	(52, 510)
2-Hexenoic acid	(137)
Isocrotonic acid	(135)
Lactal	(48)
Linoleic acid	(409)
Methyl dihydroxycholenate	(162)
3-Methylglucal	(314)
Oleic acid	(394)
2-Pentenoic acid	(137)
cis-Phenylbutadiene	(376)
Rhamnal	(52, 53)
Ricinelaidic acid	(38)
Ricinoleic acid	(38)
1,2,3,4-Tetracetyl-1,2-glucosene	(494)
Triacetylgalactal	(315)
Triacetylglucal	(314, 510)

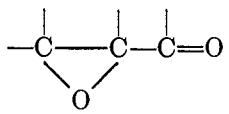
been converted to α-glycols or to hydroxybenzoates by oxidation with perbenzoic acid are listed in table 4.

3. Miscellaneous

The peracid oxidation of compounds containing aromatic double bonds has also been studied. Henderson and Boyd (251) treated numerous phenols with 30 per cent hydrogen peroxide in acetic acid solution and obtained quinones or dihydric and tetrahydric phenols. The initial stage of the reaction seems to involve oxidation at a double bond. Phenols studied were phenol, *o*-, *m*-, and

p-cresols, *p-tert*-butylphenol, 3,5-diethylphenol, carvacrol, and thymol. They also reported that benzene, toluene, and 1,3-diethylbenzene are not attacked but that naphthalene, anthracene, and phenanthrene are readily oxidized yielding phthalic acid, anthraquinone, and phenanthraquinone, respectively. Recently Greenspan (232), employing concentrated peracetic acid, obtained anthraquinone in good yield from anthracene. Charrier and Moggi (171) duplicated some of the work of Henderson and Boyd (251) and confirmed the fact that hydrogen peroxide in acetic acid solution converts naphthalene and anthracene to phthalic acid and anthraquinone, respectively, but they reported that benzene is slowly oxidized to carbon dioxide, water, and a resinous material, and that phenanthrene is converted to diphenic acid (phenanthraquinone is postulated as an intermediate). They also demonstrated that 2-*N*-phenyl-α,β-naphthotriazole yields *o,o'*-2-*N*-phenyltriazolephenyldicarboxylic acid. Although Böeseken and Slooff (110) confirmed the fact that phenanthrene yields diphenic acid on oxidation with peracetic acid, they reported that naphthalene is converted to *o*-carboxyallocinnamic acid and not to *o*-phthalic acid, that benzene is stable toward this oxidizing agent, and that anthracene, although it reacts, does not yield anthraquinone. In view of Greenspan's recent work with anthracene (232), this last observation of Böeseken and Slooff (110) cannot be accepted. Later, Böeseken and Engelberts (83, 96a) confirmed the fact that benzene is not attacked by peracetic acid, and showed that phenol is converted to *cis,cis*-muconic acid (*o*-quinone intermediate) in excellent yield and that some benzoquinone is also obtained. Catechol (83) is also converted to muconic acid, as well as to carbon dioxide and fumaric acid, and hydroquinone yields quinhydrone and fumaric acid. α-Naphthol (118) is converted in poor yields to *o*-carboxyallocinnamic acid, coumarin, α-naphthoquinone, and a resin reported to be a polymer of α-naphthoquinone oxide. β-Naphthol (63, 118), however, is converted to *o*-carboxyallocinnamic acid in good yield, some tetrahydroxynaphthalene and an acid ($C_{20}H_{12}O_4$) also being formed. Greenspan (232) has recently confirmed the fact that *o*-carboxyallocinnamic acid is formed in good yield when β-naphthol is oxidized with peracetic acid. In a similar manner, Bigiavi and Cerchiai (63) obtained *o*-carboxyallocinnamic acid from 1-benzeneazo-2-naphthol on oxidation with cold peracetic acid or with hydrogen peroxide and acetic acid, and obtained dihydroisocoumarincarboxylic acid when hot peracetic acid was employed. Grundmann and Trischmann (236) reported that *o*-coumaric acid is converted to *cis,cis*-muconic acid in small yield by peracetic acid and that 2,2'-dihydroxydiphenyl yields two products which are probably 2'-hydroxy-2-phenylquinone and α-(hydroxyphenyl)muconic lactone. 1,8-Dihydroxynaphthalene (112) is resinified by peracetic acid, but its monomethyl ether yields a mixture of 8-methoxy-α-naphthoquinone and a dehydration product of methoxy-3-carboxyallocinnamic acid. *p*-Cymene (222) is oxidized in poor yields to carvacrol, thymohydroquinone, and thymoquinone by hydrogen peroxide and acetic acid. When ferrous sulfate is added to the peracetic acid, *p*-isopropylbenzaldehyde is obtained. With an excess of peracid, the quinones which form in the reactions just described are cleaved to dibasic acids (Section III, E).

The peracid oxidation of unsaturated compounds in which the double bond is adjacent to a carbonyl group (—C=C—C=O) represents an unusual reaction. In the oxidation of such compounds, an oxygen atom is introduced between the carbonyl group and the ethylenic carbon atom (—C=C—O—C=O). Böeseken and coworkers (100, 102, 113), who are apparently the only investigators who studied this reaction, converted benzalacetone to β-phenylvinyl acetate (acetate of enolized phenylacetaldehyde), and obtained similar oxidation products from α-methyl-α-benzalacetone and from benzalmethyl ethyl ketone. The formation of the oxidation products is not a secondary reaction resulting from the isomerization of an oxirane compound,



since such a compound, prepared from benzalacetone by oxidation with alkaline hydrogen peroxide (558), is unaffected by peracetic acid under the reaction conditions employed.

In two cases (benzaldehyde phenylhydrazone and furfural phenylhydrazone, table 1), the carbon–nitrogen double bond has been oxidized to the oxirane group by perbenzoic acid (54) but in other instances a different type of reaction has been reported. Bergmann, Ulpts, and Witte (54) oxidized benzanil with perbenzoic acid in ether solution and obtained nitrobenzene and benzaldehyde. Benzophenone phenylhydrazone, under similar conditions, yields benzophenone and benzoic acid. Botvinnik and coworkers (128, 129) studied the perbenzoic acid oxidation of carbon–nitrogen double bonds in imidazoles and similar substances, and reported marked degradation of the molecule.

A limited amount of work has been published on the oxidation of acetylenic compounds. When reaction occurs, these substances are cleaved to shorter chain-length fragments. Böeseken and Slooff (109) obtained good yields of pelargonic and azelaic acids from stearolic (9-octadecynoic) acid by oxidation with peracetic acid. 9-Hendecynoic acid is reported to yield suberic and formic acids, and 10-hendecynoic acid yields sebacic acid. They reported that acetylene and phenylacetylene do not react with peracetic acid, but Prileschajew (429) reported that phenylacetic acid is obtained from phenylacetylene by oxidation with perbenzoic acid.

Rubber is readily oxidized at −20°C. to +145°C. by organic peracids, including performic, peracetic, perpropionic, monochloroperacetic, dichloroperacetic, monobromoperacetic, and monobromoperpropionic acids (71, 337), or with hydrogen peroxide and acetic (337) or formic acid (71). No definite products were isolated, however.

Camphene (256) and β-pinene (253), on treatment with hydrogen peroxide and acetic acid at 60°C., yield many products consisting of acids, ketones, aldehydes, and alcohols. α-Pinene (257), however, when similarly treated, yields α-terpineol

as the main oxidation product. Bornylene (252) is converted to a mixture of acids, esters, and aldehydes, but no ketones are formed. Sabinene (254) and sabinol (255) yield two isomeric products which appear to be glycol anhydrides.

Diallyl has been reported to react normally with perbenzoic acid, but the expected dioxirane compound could not be isolated (84). On hydrolysis the oxidation products yield 2,5-di(hydroxymethyl)tetrahydrofuran.

In the peracid oxidation of furan and its derivatives, such as furfural, 2-methylfuran, and furfuryl alcohol, the major reaction is the formation of resins (117), but small quantities of formic, maleic, and aldehydomalic acids, and the anhydride of β-acetyllactic acid are also formed. Böeseken and coworkers (117) have concluded, therefore, that the initial oxidation products are labile oxirane compounds, which rapidly resinify to a great extent but also undergo cleavage and hydrolysis, yielding the identifiable products.

Komada (305) studied the oxidation of aminopyrine and antipyrine with perbenzoic acid and reported that the expected products are not obtained. Thiopyrine (306), however, yields a diepoxy derivative.

Elm (203) studied the perbenzoic acid oxidation of trilinolenin and reported that only six of the nine double bonds are attacked, and that keto rather than oxirane compounds are formed. No evidence was presented for this conclusion.

Methoxyethyl vinyl ether (273) is converted to the dimer of ethyl 2-methoxyglycoloside by perbenzoic acid in chloroform solution. 1-Phenyl-1-(2-biphenyl)-ethylene (132) adds two atoms of oxygen but the product is unidentified. Under certain conditions 1,1-diphenylethylene yields diphenylacetaldehyde (390). Methoxymethyldihydroneostrychnine (139, 166) adds two atoms of oxygen, yielding methoxymethylchanodihydrostrychnone.

Peracetic acid converts diisobutylene to an unsaturated alcohol, a glycol, and high-boiling products (160, 260). Vinyl halide polysulfones (339) are polymerized by perbenzoic or peracetic acid, and acetylursolic acid (274) is converted to a mixture of many products when treated at the boiling point with 30 per cent hydrogen peroxide and acetic acid.

Vinet and Meunier (548, 549) reported that, contrary to the observation of Karrer and Jucker (286, 289; table 2), vitamin A or its acetate on oxidation with monoperphthalic acid in ether solution yields a secondary alcohol and not an oxirane compound. Gridgeman and coworkers (234) oxidized β-carotene with perbenzoic acid in chloroform solution and reported the formation of a five-membered oxygen-containing ring.

Daniels and Levy (179a) prepared esters of valerolactone by treating esters of alkenylmalonic acids with peracids in the presence of strong mineral acid catalysts.

B. OXIDATION OF ORGANIC SULFUR COMPOUNDS

One of the most efficient and widely used reactions of organic peracids is the oxidation of organic sulfides and mercaptans to sulfoxides and sulfones. These reactions usually proceed at convenient temperatures, are rapid, and in most cases give very high or even quantitative yields of product. Perhaps the earliest

application of this reaction was reported by Hinsberg (266), who obtained good yields of the corresponding sulfoxides by the oxidation of dibenzyl sulfide, di-*p*-acetaminophenyl sulfide, diphenyl disulfide, and dibenzyl disulfide with hydrogen peroxide in acetic acid solution. With larger quantities of hydrogen peroxide, sulfones are obtained. Furthermore, the sulfoxides can be quantitatively converted to the sulfones by the same oxidant mixture. It is not essential to employ an organic acid as the solvent and oxygen-carrier (peracid intermediate) for these reactions, and inert solvents may be used (226, 457, 537), but the reactions are more satisfactory when an organic peracid (preferably prepared and utilized *in situ*) is the oxidant (228). Table 5 gives an alphabetical list of organic sulfur compounds converted to sulfoxides and/or sulfones by organic peracids.

Alkyl thiolsulfinates have been prepared (485) by the oxidation of aliphatic disulfides, such as dimethyl, diethyl, dipropyl, dibutyl, diamyl, and diallyl disulfides, with organic peracids. Perbenzoic acid is generally employed, but peracetic, perfuroic, perphthalic, and percamphoric acids can also be used. Perlauric acid, however, is not so satisfactory as the others.

Pomerantz and Connor (418) converted a series of α-alkylthioamides to the corresponding α-alkylsulfonamides in good yield by oxidation with a mixture of hydrogen peroxide, acetic acid, and acetic anhydride.

Surprisingly, 1,2-bis(2-diethylaminoethylmercapto)ethane hydrochloride, 1,2-bis(2-dibutylaminoethylmercapto)ethane hydrochloride, and 1,2-bis[2-(1-piperidyl)ethylmercapto]ethane hydrochloride are converted to the sulfone or sulfonic acid, with the loss of two methylene groups, when hydrogen peroxide and acetic acid at the boiling point are employed as the oxidizing agent (424).

C. OXIDATION OF ORGANIC NITROGEN COMPOUNDS

The oxidation of organic nitrogen compounds with organic peracids falls into three main classes: (*1*) oxidation of amines to nitroso, azo, azoxy, and nitro compounds, (*2*) oxidation of azo compounds to azoxy compounds, and (*3*) oxidation of amines to amine oxides.

1. Oxidation of amines to nitroso, azo, azoxy, and nitro compounds

Baeyer and Villiger (31, 33) observed that on oxidation with perbenzoic or monoperphthalic acid aniline is converted to nitrosobenzene, but yields were not reported. Prileschajew (425), however, reported that aniline yields azobenzene when treated with an equimolar quantity of perbenzoic acid and that nitrosobenzene and a little nitrobenzene are obtained when double the quantity of perbenzoic acid is employed. *o*-Toluidine yields *o*-nitrotoluene when similarly treated. Again, yields were not reported. Prileschajew also studied the oxidation of azoxybenzene and methylaniline, but did not report the products obtained.

D'Ans and Kneip (189) have stated that primary amines are converted to nitroso compounds on oxidation with peracids in the cold, but with concentrated peracids and without cooling the reaction mixture nitro compounds are obtained. By varying the quantity of peracid and the reaction conditions, azo and azoxy compounds can also be prepared. D'Ans and Kneip obtained fair yields of both

TABLE 5

Organic sulfur compounds converted to sulfoxides and/or sulfones by oxidation with organic peracids

SULFUR COMPOUND	REFERENCES
2-Acetylamino-4-methyl-4′-nitro-5-thiazolylphenyl sulfide	(35)
2-Acetylamino-4′-nitro-5-thiazolylphenyl sulfide	(35)
2-Acetylamino-4′-nitro-5-thiodiazolylphenyl sulfide	(35)
2-Acetylmethylamino-4-methyl-4′-nitro-5-thiazolylphenyl sulfide	(35)
ω-Alkylmercapto fatty acids	(443)
4-Aminodiphenyl sulfide	(229)
Benzyl carboxymethyl sulfide	(393)
8-Benzylthiocaffeine	(331b)
1,2-Bis(2-benzoxyethylmercapto)ethane	(423)
1,2-Bis(2-chloroethylmercapto)ethane	(423)
Bis(ethylthio)methane	(121, 477)
1,2-Bis(2-hydroxyethylmercapto)ethane	(423)
Bis(2-nitro-1-naphthyl)sulfide	(223a)
Bis(4-nitro-1-naphthyl)sulfide	(223a)
4-Bromo-4′-nitrodiphenyl sulfide	(5)
2-Bromo-8-nitrothiaxanthene	(4a)
n-Butyl 2-chloroethyl sulfide	(155a)
Isobutyl 2-chloroethyl sulfide	(155a)
Butyl 2-nitropropyl sulfide	(245a)
8-*n*-Butylthiocaffeine	(331b)
n-Butyl *p*-tolyl sulfide	(228)
Carboxymethyl 2-nitroethyl sulfide	(245a)
Casein	(524)
2′-Chloro-4-aminodiphenyl sulfide	(229)
3′-Chloro-4-aminodiphenyl sulfide	(229)
4′-Chloro-4-aminodiphenyl sulfide	(229)
p-Chlorobenzyl sulfidoacetic acid	(393)
4′-Chloro-2,4-diaminodiphenyl sulfide	(229)
3′-Chloro-2,4-dinitrodiphenyl sulfide	(229)
4′-Chloro-2,4-dinitrodiphenyl sulfide	(229)
2-(2-Chloroethylmercapto)ethyl ether	(422)
2-Chloroethyl *p*-tolyl sulfide	(228)
2-Chloro-2′-methylthiodiethyl sulfide	(154)
2′-Chloro-4-nitrodiphenyl sulfide	(229)
3′-Chloro-4-nitrodiphenyl sulfide	(229)
4′-Chloro-4-nitrodiphenyl sulfide	(229)
1-Chlorovinyl 2-chloroethyl sulfide	(331)
2-Chlorovinyl 2-chloroethyl sulfide	(331)
2-Crotonyl-4′-nitro-5-thiazolylphenyl sulfide	(35)
Cystine	(477a, 526, 527, 528, 529, 530)
2,8-Diacetamidothioxanthone	(6)
Di(*p*-acetylaminophenyl) sulfide	(266)
Diallyl sulfide	(330)
2,8-Diaminodibenzothiophene (tetraacetyl derivative)	(389)
Dibenzyl disulfide	(266)
Dibenzyl sulfide	(21, 122, 266, 328, 329, 457)

TABLE 5—*Continued*

SULFUR COMPOUND	REFERENCES
2,8-Dibromodibenzothiophene	(389)
2,2′-Dibromodiethyl sulfide	(330)
Di(*p*-bromophenyl) sulfide	(87, 457)
Di(2,4-dichlorobenzyl) sulfide	(393)
1,1′-Dichlorodiethyl sulfide	(330)
2,2′-Dichlorodiethyl sulfide	(328, 329)
1,1′-Dichlorodimethyl sulfide	(328, 330)
4-(2-Diethylaminoethylamino)phenyl 4-nitrophenyl sulfide	(434)
Di-*n*-hexadecyl sulfide	(457)
2,2′-Dihydroxydiethyl sulfide (thiodiglycol)	(330, 421)
Di-(*p*-methoxyphenyl) sulfide	(457)
4-(2,5-Dimethyl-1-pyrryl)diphenyl sulfide	(229)
2,2′-Dimethylsulfonyldiethyl sulfide	(154)
2,2′-Dimethylthiodiethyl sulfide	(154, 168, 342)
1,2-Dimethylthioethane	(154, 168)
2,2′-Di(2-methylthioethylthio)diethyl ether	(342)
2,2′-Di(2-methylthioethylthio)diethyl sulfide	(342)
1,2-Di(2-methylthioethylthio)ethane	(342)
Di(*p*-nitrobenzyl) sulfide	(457)
Di(nitro-*tert*-butyl) sulfide	(245a)
Di(2-nitro-1-methylpropyl) sulfide	(245a)
2,8-Dinitro-10-methylthiaxanthenol	(6)
2,8-Dinitrothiaxanthone	(6)
Diphenyl disulfide	(266)
Di(2-phenylethyl) sulfide	(457)
Diphenylmethyl α-naphthyl sulfide	(300)
Diphenylmethyl phenyl sulfide	(300)
Diphenyl sulfide	(87, 328, 329, 457)
Di(β-pyridiniummethyl) sulfide dichloride	(496)
Di(*p*-tolyl) sulfide	(457)
Divinyl sulfide	(330)
Dodecyl 2,3-dihydroxypropyl sulfide	(298)
Ethyl benzyl sulfide	(121)
Ethyl *n*-butyl sulfide	(228)
Ethyl chloromethyl sulfide	(121, 122)
Ethyl ethoxymethyl sulfide	(121)
Ethylene-sulfur chloride reaction product	(404)
Ethyl oleyl sulfide	(298)
8-Ethylthiocaffeine	(331b)
4-(2-Hydroxyethylthiol)-2-aminobutyric acid	(490)
2-Hydroxyethyl naphthenyl sulfides	(298)
4-Iodo-4′-nitrodiphenyl sulfide	(5)
2-Iodo-8-nitrothiaxanthene	(4a)
Methionine	(525)
6-Methoxy-8-(4-*quinazolonyl*)phenyl sulfide	(202)
2′-Methyl-4-aminodiphenyl sulfide	(229)
3′-Methyl-4-aminodiphenyl sulfide	(229)
4-Methyl-4-aminodiphenyl sulfide	(229)
Methyl 2-chloroethyl sulfide	(154, 155a)

TABLE 5—*Concluded*

SULFUR COMPOUND	REFERENCES
3′-Methyl-2,4-diaminodiphenyl sulfide	(229)
3′-Methyl-4-(2,5-dimethyl-1-pyrryl)diphenyl sulfide	(229)
4′-Methyl-4-(2,5-dimethyl-1-pyrryl)diphenyl sulfide	(229)
3′-Methyl-2,4-dinitrodiphenyl sulfide	(229)
2′-Methyl-2-nitrodiphenyl sulfide	(229)
2′-Methyl-4-nitrodiphenyl sulfide	(229)
3′-Methyl-4-nitrodiphenyl sulfide	(229)
4′-Methyl-4-nitrodiphenyl sulfide	(229)
Methyl 2-nitroethyl sulfide	(245a)
Methyl 2-nitropropyl sulfide	(245a)
8-Methylthiocaffeine	(331b)
Methyl *p*-tolyl sulfide	(228)
Mustard gas (Levinstein)	(223)
5-Nitro-2-(*p*-bromothiophenoxy)benzoic acid	(4a)
4-Nitrodiphenyl sulfide	(229)
5-Nitro-2-(*p*-iodothiophenoxy)benzoic acid	(4a)
6-Nitro-2-methylthioxanthene	(163a)
7-Nitro-2-methylthioxanthene	(163a)
6-Nitro-2-methylthioxanthone	(163a)
7-Nitro-2-methylthioxanthone	(163a)
5-Nitro-2-(*p*-nitrothiophenoxy)acetophenone	(6)
p-Nitrophenyl octyl sulfide	(159)
2-Nitro-4-(*p*-tolylthio)benzaldehyde	(163a)
4-Nitro-2-(*p*-tolylthio)benzaldehyde	(163a)
Phenyl 2-hydroxy-3-chloropropyl sulfide	(388)
Phenyl 2-hydroxycyclohexyl sulfide	(388)
Phenyl octyl sulfide	(159)
8-Phenylthiocaffeine	(331b)
2-Phenylthio-2′-methylthiodiethyl sulfide	(154)
1-Phenylthio-2-methylthioethane	(154, 168)
4′-Isopropyl-4-aminodiphenyl sulfide	(229)
4′-Isopropyl-2,4-dinitrodiphenyl sulfide	(229)
4′-Isopropyl-4-nitrodiphenyl sulfide	(229)
8-*n*-Propylthiocaffeine	(331b)
8-Isopropylthiocaffeine	(331b)
n-Propyl *p*-tolyl sulfide	(228)
Pseudomethionine	(490)
2-Succinylamino-4′-nitro-5-thiazolylphenyl sulfide	(35)
Thianthrene	(116)
Thioxanthene	(265a)
Thioxanthone	(265a)
p-Tolyl 2-chloroethyl sulfide	(155a)
Vinyl thiocresyl ethers	(537)

nitrosobenzene (50 per cent) and azoxybenzene (35 per cent) by the oxidation of aniline in an aqueous system with peracetic acid added dropwise, but when the peracid is added in one portion, a 70 per cent yield of nitrosobenzene and a 25 per cent yield of azoxybenzene are obtained. In similar reactions (184, 189)

p-toluidine yields nitrosotoluene, azotoluene, and azoxytoluene; *m*- and *p*-nitroanilines yield nitronitrosobenzene and dinitroazoxybenzene; and anthranilic acid in alcohol solution yields nitrosobenzoic acid. Recently Greenspan (232) obtained an 85 per cent yield of azoxybenzene and a 15 per cent yield of nitrobenzene from aniline by oxidation with 45 per cent peracetic acid. Azo compounds are presumably the precursors of the azoxy compounds.

Bigiavi (57) and Bigiavi and Albanese (60) reported that, unlike the free amino compounds, acetyl derivatives of simple primary aromatic amines are converted to nitro derivatives only. Compounds studied were the acetyl derivatives of aniline, *p*-bromoaniline, *p*-nitroaniline, *p*-toluidine, pseudocumidene, and isomeric *p*-aminoazobenzenes.

Gambarjan (225) obtained an orange-red compound, melting at 138–142°C., when diphenylamine was oxidized with perbenzoic acid.

2. Oxidation of azo compounds to azoxy compounds

One of the most clean-cut reactions of organic peracids is the conversion of azo compounds to azoxy compounds. This reaction proceeds readily under mild conditions, and quantitative yields are frequently obtained. In most cases, hydrogen peroxide and acetic acid have been employed, but in some, previously prepared peracetic acid has been used. This reaction was explored from 1910 through 1934 by Angeli, Bigiavi, D'Ans, and their coworkers. Azo compounds converted to azoxy compounds are listed alphabetically in table 6.

3. Oxidation of amines to amine oxides

Amine oxides can be prepared in good yields from amines by reaction with organic peracids. Monopersulfuric acid (Caro's acid) is not satisfactory for this reaction, and aqueous hydrogen peroxide reacts very slowly and gives low yields of *N*-oxide (347). Although organic peracids do not yield the *N*-oxide directly, and salts of the carboxylic acids are formed thereby requiring further processing, the *N*-oxides are usually purified more easily than when hydrogen peroxide alone is employed (42). Amines converted to *N*-oxides by oxidation with organic peracids (usually perbenzoic and monoperphthalic acids) are listed alphabetically in table 7.

D. OXIDATION OF ALDEHYDES

Aldehydes are usually converted to the corresponding acids in excellent yield by organic peracids (1, 31, 144, 163a, 189, 219, 332, 333, 440, 463, 511, 561, 570, 578). This oxidation reaction appears to be a general one, with the exception of the oxidation of phenolic and etherified phenolic aldehydes.

Phenolic aldehydes, as well as etherified phenolic aldehydes, undergo a more complex reaction, in which the aldehyde group is converted to the phenolic hydroxyl group (or the acylated hydroxyl group). This reaction appears to have been discovered by Dakin (179), who obtained an abundant yield of catechol from *o*-hydroxybenzaldehyde on oxidation with perbenzoic acid. D'Ans and Kneip (189) showed that *p*-hydroxybenzaldehyde behaves similarly on oxidation

with peracetic acid, yielding hydroquinone and its oxidation products quinhydrone and quinone. Böeseken and coworkers (91, 97) oxidized various etherified phenolic aldehydes, and demonstrated that peracetic acid converts the aldehyde group to the phenolic hydroxyl group. Compounds studied were piperonal (91),

TABLE 6

Azo compounds converted to azoxy compounds by oxidation with organic peracids

AZO COMPOUND	REFERENCES
4-Acetoxyazobenzene	(9)
4-Acetylaminoazobenzene	(57, 59, 400)
4-Acetylazobenzene	(10)
4-Aminoazobenzene	(400, 540)
Azobenzene	(7, 189)
4-Benzoxyazobenzene	(58)
4-Benzoylazobenzene	(10)
4-Bromoazobenzene	(18)
p-Bromoazo-*o*-toluene	(19)
4-Bromohydrazobenzene	(9)
2-Bromo-4-nitroazobenzene	(61)
4-Bromo-4′-nitroazobenzene	(18)
4-Carboxyazobenzene	(20)
Cyanomethylazobenzene	(10)
4,4′-Diacetoxyazobenzene	(62)
Diazoresin (from aniline)	(17)
Dibenzoyl-*o*-azophenol	(67)
4,4′-Dibromoazobenzene	(18)
2,4-Dihydroxyazobenzene	(65)
2,5-Dihydroxyazobenzene (benzoyl and acetyl derivatives)	(64)
4,4′-Dihydroxyazobenzene	(9, 14, 62)
3,3′-Dinitroazobenzene	(189)
4,4′-Dinitroazobenzene	(189)
4-Hydroxyazobenzene	(58, 68)
2-Hydroxy-5-methylazobenzene	(69)
4-Methylazobenzene	(70)
4-Nitroazobenzene	(15, 16)
N,*N*′-Di-2-pyridyl-4,4′-hydrazobenzenedisulfonamide	(333a)
Phenylazocarboxamide	(12, 13)
Polyazo compounds	(8)
Quinone phenylhydrazones (benzoyl derivative)	(58)
4-Sulfoazobenzene	(20)
2,4,6-Trinitroazobenzene	(20)
2,3,4-Trihydroxyazobenzene (and tribenzoate)	(66)

3,4-dimethoxyvanillin (97), ethylvanillin (97), 3-ethoxy-4-methoxybenzaldehyde (97), 3,4-diethoxybenzaldehyde (97), 3-methoxy-4-butoxybenzaldehyde (97), and 3-ethoxy-4-butoxybenzaldehyde (97). Formic acid is also obtained as an oxidation product in these reactions, but its origin was not explained. Some years later, the reaction was studied further by von Wacek and coworkers (550, 550a, 551, 552), who showed that hydrogen peroxide–acetic acid, as well as preformed peracetic

TABLE 7

Amines converted to amine oxides by oxidation with organic peracids

AMINE	REFERENCES
4-*p*-Acetamidophenylsulfonylpyridine	(159)
Benzo-[*f*]-quinoline	(25)
7-Chloroisoquinoline	(461)
6-Chloroquinoline	(25)
Cinchonidine	(42)
Cinchonine	(42)
2,5-Di-*sec*-butylpyrazine	(390a)
Dihydrostrychnine	(307)
Dimethylaniline	(45a)
2,5-Dimethylpyrazine	(390a)
2,3-Diphenylquinoxaline	(331a, 336a)
Ethylallylaniline	(348a)
Ethylbis(2-chloroethyl)amine	(495)
1-Hydroxyphenazine	(171a)
Isoquinoline	(348)
6-Methoxy-8-acetylaminoquinoline	(230)
6-Methoxyisoquinoline	(461)
6-Methoxyquinoline	(541)
Methylallylaniline	(299a, 347)
2-Methyl-3-*n*-amylquinoxaline	(340a)
Methylbenzylaniline	(299a, 348a)
Methylbenzylaniline picrate	(299a)
Methylbis(2-chloroethyl)amine	(495)
Methylcinnamylaniline	(299a)
Methylcrotylaniline	(299a)
Methyldiethanolamine	(495)
Methyldiphenylamine	(45a)
2-Methyl-3-phenyl-1,2-naphthoquinoxaline	(336a)
2-Methylquinoxaline	(340a)
Neostrychnine	(166)
1,2-Naphthophenazine	(336a)
5-Nitroquinoline	(230, 560)
6-Nitroquinoline	(25)
o,*m*,*p*-Phenanthrolines	(295a, 331a)
Phenazine	(171a, 340a, 438a)
Pyridine	(348)
Quinaldine	(348b)
Quinidine	(42)
Quinine	(42)
Quinoline	(348)
Quinoxaline	(340a)
Strychnine	(307)
1,2,3,4-Tetrahydrophenazine	(340a)
2,4,6-Triphenylpyridine	(348)
Tris(2-chloroethyl)amine	(495)

acid, can be employed and that the reaction is also applicable to appropriately substituted aromatic ketones. Since formyl esters are obtained in a few of the

reactions (550, 550a), it was concluded that this product is an intermediate and on hydrolytic cleavage yields the phenol and formic acid. The reaction apparently involves the insertion of an oxygen atom between the carbon atom of the carbonyl group and the aromatic carbon atom to which it is attached, and is analogous to the reaction of peracids with α,β-unsaturated aliphatic ketones discussed earlier (100, 102, 113). Compounds oxidized by von Wacek and coworkers were salicylaldehyde (550, 550a, 551, 552), 6-hydroxy-3-methoxybenzaldehyde (550), 2-hydroxy-4-methylbenzaldehyde (550), *m*- and *p*-hydroxybenzaldehydes (550), veratraldehyde (550), salicylaldehyde methyl ether (550), and *p*-methoxyacetophenone (550), the expected phenols being obtained generally in excellent yield. Anisaldehyde, however, is converted to anisic acid in good yield (189).

E. OXIDATION OF KETONES AND QUINONES

In general, monoketones are unaffected by organic peracids, but in a few cases, mostly cyclic and methyl ketones, oxidation has been reported. Baeyer and Villiger (31) obtained mentholactone from menthone, Burckhardt and Reichstein (157, 158) converted some sterol ketones to lactones, and Sarett (477b) converted several methyl ketones of the pregnane series to acetoxy derivatives on oxidation with perbenzoic acid. This reaction is similar to the Baeyer oxidation of ketones with monopersulfuric acid (Caro's acid) (30). As mentioned before, however, *p*-methoxyacetophenone is converted to hydroquinone monomethyl ether by peracetic acid (550).

Diketones and quinones are cleaved to carboxylic acids by organic peracids. Perkin (403) showed that hydrogen peroxide and acetic acid react readily with 1,2-diketones and with substances containing the quinonoid structure. Benzil and phenanthraquinone are converted to benzoic and diphenic acids, respectively (403). Aurine yields *p*-hydroxybenzoic acid and hydroquinone, the latter being oxidized to benzoquinone (403). Brazilein and trimethylbrazilein yield acids having the formulas $C_{16}H_{14}O_9$ and $C_{19}H_{20}O_8$, respectively (403). Charrier and Beretta (169) oxidized acenaphthenequinone and phenanthraquinone to diphenic acids, β-naphthoquinone to phthalic acid, and 2-*N*-phenyl-1,2-naphthotriazolequinone and 2-*N*-*p*-chlorophenyl-1,2-naphthotriazolequinone to the anticipated dibasic acids with hydrogen peroxide–acetic acid. Böeseken and Slooff (108), however, obtained *o*-carboxyallocinnamic acid by oxidizing β-naphthoquinone with peracetic acid, and Karrer and Schneider (291) obtained a similar result with perbenzoic acid. *o*-Benzoquinone is similarly cleaved, yielding *cis,cis*-muconic acid (107, 108), and on oxidation with monoperphthalic acid in ether solution, tetrabromo-*o*-quinone yields the lactone of tribromomucic acid (291).

On oxidation with peracetic acid, 9,10-diketostearic acid is quantitatively converted to azelaic and pelargonic acids (108). Diacetyl and benzil behave similarly, yielding acetic and benzoic acids, respectively. In the oxidation of the 1,2-diketone ($[C_6H_5(CH{=}CH)_2CO]_2$) with monoperphthalic acid, Karrer and coworkers (282) obtained a product ($C_{22}H_{18}O_3$) whose structure was not established and a small quantity of 5-phenylpentadienoic acid.

1,3-Diketones are also cleaved by peracetic acid (101), yielding an acid and an

alcohol in the absence of excess peracetic acid, and 2 moles of acid when an excess of peracetic acid is employed. 1,3-Diketones having the group —$COCH_2CO$— are more easily oxidized than the monosubstituted diketones —COCHRCO—. Diketones of the general formula RCOCHR'COR", in which R is methyl, ethyl, amyl, phenyl, or *p*-nitrophenyl, R' is hydrogen, methyl, or benzyl, and R" is methyl, methoxyl, or ethoxyl have been studied by Böeseken and Slooff (101). These workers concluded that the reaction involves enol formation first, followed by addition of oxygen at the double bond, yielding an oxirane compound. This then undergoes ring opening, with shifting of the group R', followed by hydrolysis or acetolysis (82).

F. OXIDATION OF ORGANIC IODINE COMPOUNDS

Organic iodine compounds when treated with peracetic acid usually yield diacetates of the corresponding iodoso compounds, whereas with perbenzoic acid iodoxy compounds are usually obtained (105, 106). On treatment with perbenzoic acid, the iodosoacetates are converted to iodoxy compounds. Böeseken and Schneider (104, 105, 106) obtained diacetates of the corresponding iodoso compounds by the oxidation of iodobenzene (104, 105, 106), diiodobenzenes (105, 106), iodotoluenes (105, 106), iodobenzoic acids (105, 106, 119), iodobenzenesulfonic acids (105), *o*- and *m*-iodonitrobenzenes (105, 106), and 1,2-diiodoethylene (105) with peracetic acid. When perbenzoic acid is used as the oxidizing agent, the iodoxy compounds are obtained, with the exception of *o*-iodobenzoic acid and *p*-iodobenzenesulfonic acid, which yield iodoso compounds (105). Mono- and di-iodofumaric acids and iodoacrylic acid yield the iodoso compounds (106), iodoform is converted to iodine and iodine pentoxide, and diiodoacetylene is converted to tetraiodoethylene (106). Surprisingly, on oxidation with peracetic acid in chloroform solution 1,2-diiodo-1,2-diphenylethylene (1,2-diiodostilbene) yields 1,2-dichloro-1,2-diphenyl-1,2-epoxyethane (1,2-dichlorostilbene oxide), thus indicating that the solvent may play a role in some peracid oxidations (106).

The oxidation of iodobenzene with peracetic acid has also been studied by Arbuzow (21), who demonstrated that with dilute peracetic acid good yields of the diacetate of iodosobenzene are obtained but with 90 per cent peracetic acid in ether solution mixtures of iodoxybenzene and of the diacetate of iodosobenzene are obtained. By employing 50 per cent peracetic acid and sodium bicarbonate in the reaction, iodoxybenzene is obtained. With perbenzoic acid, iodobenzene yields the benzoyl derivative of iodosobenzene (21). When iodoxybenzene is treated with 50 per cent peracetic acid, the diacetate of iodosobenzene is obtained (21).

Jorissen and Dekking studied the oxidation of iodobenzene dissolved in acetaldehyde (277) or in benzaldehyde (276) through which oxygen was being passed. Peracetic or perbenzoic acid (prepared and utilized *in situ*) was assumed to be the oxidizing agent. In acetaldehyde solution iodoxybenzene was obtained, whereas in benzaldehyde solution iodosobenzene was obtained. These results are not in accord with the results of Böeseken and Schneider (105, 106).

G. MISCELLANEOUS

The oxidation of thiopyrine to the trioxide by peracetic acid has been reported by D'Ans and Kneip (189), although the structure of the product was not given.

Arbuzow (21) oxidized diphenylselenide with peracetic acid in ether and also in acetic acid solution. With dilute peracetic acid, the hydrate of diphenylselenoxide as well as its monoacetate was obtained, and with 90 per cent peracetic acid, diphenylselenone was obtained. With perbenzoic acid in ether solution, diphenylselenide was converted to diphenylselenone (21). Yields in these reactions were good. Triphenylphosphine oxide was also obtained in good yield by the oxidation of triphenylphosphine with dilute peracetic acid (21).

Medvedev and Alekseeva (344) oxidized hexaphenylethane with perbenzoic acid and obtained triphenylmethylperoxide and two isomers of the formula $C_{38}H_{30}O$, one of them being $(C_6H_5)_2C(OC_6H_5)C(C_6H_5)_3$.

By oxidizing several carbenium perchlorates with hydrogen peroxide and acetic acid Dilthey, Quint, and Dierichs (193) obtained cleavage of carbon-to-carbon bonds, with the formation of ketones and phenols.

The action of perbenzoic acid on numerous polycyclic aromatic compounds was studied by Eckhardt (198), who reported that methylcholanthrene and 3,4-benzopyrene absorb oxygen most rapidly. Other compounds studied were pyrene, benzopyrene-5-aldehyde, 5-nitrobenzopyrene, 4- and 6-methyl-1,2-benzanthracenes, 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, and anthracene. Oxidation products were not reported. Wittig and Henkel (575) observed that a large excess of perbenzoic acid converts 9,10-diphenylacenaphthylene to 1,8-dibenzoylnaphthalene.

Karrer and Trugenberger (293) oxidized the methyl ether of 3,7,4′-trimethoxy-2-phenylbenzopyrylium base with monoperphthalic acid and obtained 7,4′-dimethoxyflavonol. A complex reaction involving oxidation at the double bond as well as loss of methoxyl occurs.

Under certain conditions, polyhydric phenols are oxidized to quinones by organic peracids. Excesses of peracid must be avoided since, as mentioned earlier (Section III, E), it will attack the quinone further, yielding carboxylic acids. Perkin (403) observed that hydroquinone yields benzoquinone, and Bigiavi and de Benedetti (64) reported that benzeneazohydroquinone yields the corresponding quinone when hydrogen peroxide–acetic acid is employed as the oxidizing agent. Pratesi and Celeghini (419) reported that 2,5-bis[2,4-dimethyl-*N*-pyrryl]-3,6-dibromohydroquinone is converted to an intensely blue quinone by oxidation with perbenzoic and monoperphthalic acids, or with peroxides, such as ethyl, benzoyl, and hydrogen peroxide. In the oxidation of pyrogallol with percompounds, in the presence of peroxides, Wieland and Sutter (572) and Böeseken (82) reported that disubstituted peroxides have no effect but that peracetic and perbenzoic acids cause oxidation to occur. Products were not isolated.

An unusual reaction is the dehydrogenation of isopyrocalciferol acetate to dehydroergosterol acetate by perbenzoic acid (573a).

Tri-*n*-butylborine is quantitatively oxidized by perbenzoic acid, yielding *n*-butyl alcohol and boric acid (275).

In the thiaxanthene series, the reactive methylene group can be converted to the carbonyl group by oxidation with hydrogen peroxide and acetic acid (4a, 163a, 265a).

Attention is directed to the brief review on oxidations with organic peracids by Böeseken (81).

IV. Organic Peracids in the Determination of Structure and in the Analysis of Organic Compounds

The reaction of organic peracids with organic compounds has been employed by many investigators to determine the number of atoms of oxygen consumed per mole of organic compound. This technique has been employed either as an analytical tool or, in the determination of structure, as an additional method for confirming the presence of an oxidizable group, such as the double bond, in the molecule. The usual procedure is to add a measured quantity of a solution of the organic peracid of known concentration to the compound being studied and follow the disappearance of the peracid iodimetrically. In describing their results, some investigators have reported the number of atoms of oxygen consumed per mole of compound oxidized; others have converted oxygen consumption data to iodine numbers; and others have preferred the term "oxygen number" (378) (defined as the amount of active oxygen, supplied by perbenzoic acid, required for the oxidation of 100 g. of the substance). When pure compounds are being studied, the oxygen consumption should be reported as the number of atoms of oxygen consumed per mole of compound oxidized. Most of the investigators who have merely studied the analytical aspects of organic peracid oxidations have not isolated the oxidation products. Likewise, many of the investigators who have studied reactions with organic peracids as a preparative tool have not been concerned with the quantitative aspects of the reaction from the analytical standpoint, such as optimum times and temperatures of reaction and excess of reagent required.

An alphabetical list of substances which have been treated with organic peracids for the purpose of measuring oxygen consumption is given in table 8. In many of the cases listed quantitative reaction occurs, and the results are of considerable value, but in others insufficient reaction time has been allowed or side reactions occur, so that the data on oxygen consumption do not give a true picture of the structure of the substance. Some of the substances appear in previous tables if oxidation products have been isolated.

Determination of the total number of double bonds in olefins by peracid analysis is not so satisfactory as quantitative catalytic hydrogenation or even determination of iodine or bromine number, since oxygen consumption may be incomplete or unusually high oxygen absorption may occur as a result of side reactions with other functional groups. Determination of the rate of reaction of peracids with unsaturated compounds, particularly hydrocarbons, however, yields much reliable information regarding their structure, and this technique may become a valuable tool in structure elucidation (302, 304, 476a, 553, and Section V).

TABLE 8

Substances for which oxygen consumption measurements have been reported

SUBSTANCE	REFERENCES
Abietic acid	(357, 470)
Agnosteryl acetate	(574a)
Allyl alcohol	(360)
Amyrilene	(470, 473)
Amyrins	(473)
Anethole	(74, 357)
Anthracene	(198)
dl-Alanine	(525)
l-Arginine	(525)
dl-Aspartic acid	(525)
Atisine	(267a)
Benzalacetophenone	(580)
Benzaldehyde	(511)
Benzine	(378)
3,4-Benzopyrene	(198)
Benzopyrene-5-aldehyde	(198)
Benzoylacetone	(75)
Benzylideneglycine (barium salt)	(128)
Benzoylacetone	(128)
Bixin	(437)
Bornylene	(346, 380)
Camphene	(346)
Carotene	(436)
Carvone	(267a)
Castor oil	(488)
Chloromethyl ethyl sulfide	(122)
Chloromethyl methyl sulfide	(122)
Chloromethyl propyl sulfide	(122)
Cholesterol	(357, 360)
Cinnamalacetone	(580)
Cinnamic acid	(357)
Cinnamic aldehyde	(357)
Cinnamyl alcohol	(122)
α-Cinnamylideneacetophenone	(249)
α-Cinnamylideneacetophenone oxide	(249)
Citral	(74)
Citronellol	(74, 357, 360)
Cocoa butter	(124)
Crotonaldehyde	(580)
Crotonic acid	(357)
Cyclofenchene	(380)
Cyclohexene	(267a)
Cystine	(525)
Dehydroandrosterone	(191)
Diallyl sulfide	(122)
1,1-Dianisylethylene	(346)
Dibenzalacetone	(580)
1,2,5,6-Dibenzanthracene	(198)
Dibenzoylmethane	(75)

TABLE 8—*Continued*

SUBSTANCE	REFERENCES
Dibenzyl sulfide	(122)
Dibenzyl sulfoxide	(122)
Diethylamine	(128)
Dihydroagnosteryl acetates (α and β)	(574a)
Dihydroamyrilene	(473)
α-Dihydrolanosteryl acetate	(574a)
p-Dimethylaminoazobenzene	(11)
Dimethylcinnamylidenemalonate	(249)
Dimethyldihydroresorcinol	(128)
2,6-Dimethyl-6-octene	(511)
2,4-Dimethyl-2-pentene	(357)
1,1-Diphenylethylene	(346)
Diphenyloctatetraene	(437)
Dithioglycolic acid	(525a)
Elaidic acid	(99, 124)
α-Elemolic acid	(472b)
α-Ergostenol acetate	(574)
Ergosterol	(357, 360)
Ethyl acetoacetate	(75, 128)
Ethylamine	(128)
Ethyl benzyl sulfoxide	(122)
Ethyl eleostearate	(99)
Ethylideneacetone	(580)
Ethyl 9,12-octadecadienoate (linoleate)	(39)
Ethyl 9,12,15-octadecatrienoate (linolenate)	(488)
Ethyl oleate	(37, 39)
N-Ethylpiperidine	(267a)
Ethylthioglycolic acid	(122)
Eugenol	(74, 346)
1-α-Fenchene	(346)
Furoic acid	(360)
Geraniol	(74, 360)
Geranyl acetate	(74)
l-Glutamic acid	(525)
Glycine	(525)
Glycine anhydride dibenzyl ether	(128)
Guanidine carbonate	(128)
Hendecenoic (undecylenic) acid	(302, 476a)
1-Heptenal	(511)
2,4-Hexadiene	(357)
l-Histidine	(525)
Histidine dihydrochloride	(128, 129)
l-Hydroxyproline	(525)
Imidazole	(129)
β-Ionone	(580)
Isoatisine	(267a)
d-Isoleucine	(525)
l-Isoleucine	(525)
Isoprene	(437, 456)

TABLE 8—*Continued*

SUBSTANCE	REFERENCES
Isoeugenol	(74, 122, 346, 357, 360)
Isosafrole	(346, 357, 360)
Kerosene	(378)
Lanostenones	(195)
Lanosterols	(195, 197, 574a)
Lanosteryl acetate	(192)
l-Leucine	(525)
Limonene	(346, 357, 360, 380, 456)
Linseed oil	(124, 488)
Lubricating oils	(378)
Lycopene	(437, 456)
Lysidine	(129)
l-Lysine	(525)
Menthene	(380, 511)
8-Menthene-1,2-diol	(346)
Mesityl oxide	(357)
dl-Methionine	(525)
Methyl 3(α)-acetoxy-9-hydroxy-Δ^{11}-cholenate	(261)
4-Methyl-1,2-benzanthracene	(198)
6-Methyl-1,2-benzanthracene	(198)
α-Methylcamphene	(380)
Methylcholanthrene	(198)
Methyl cinnamylideneacetate	(249)
1-Methyl-2,2-diphenylethylene	(346)
Methyl elaidate	(99)
Methyl α-elemolate	(472b)
2-Methylimidazole	(129)
Methyl 9,12,15-octadecatrienoate (linolenate)	(99)
Methyl pimarate	(475)
Methyl piperate	(249)
5-Nitrobenzopyrene	(198)
Nonene	(357)
Octadecadienoic (linoleic) acids	(39, 99, 124, 357, 488)
Octadecatrienoic acid	(37)
Oil of calamus	(74)
Oil of caraway	(74)
Oil of cinnamon	(74)
Oil of citronella	(74)
Oil of clove	(74)
Oil of fennel	(74)
Oil of lavender	(74)
Oil of thyme	(74)
Oleic acid	(37, 39, 124, 302, 357, 476a, 488)
Olive oil	(124, 488)
Oxoisoatisine	(267a)

TABLE 8—*Concluded*

SUBSTANCE	REFERENCES
Petrolatum	(378)
dl-Phenylalanine	(525)
1-Phenyl-1-anisylethylene	(346)
α-Pimaric acid	(470)
Pinene	(122, 346, 357, 360)
Poppyseed oil	(122)
Polystyrene	(338a)
l-Proline	(525)
Pyrene	(198)
Pyrotartaric acid	(75)
Rubber (natural)	(304, 436, 476a, 553)
Rubber (synthetic)	(304, 476a, 553)
Rapeseed oil	(488)
Safflowerseed oil	(488)
Safrole	(346, 360)
d-Serine	(525)
dl-Serine	(525)
Sesame-seed oil	(124)
Sorbic acid, esters, amide, and chloride	(249)
Soybean oil	(488)
Styrene	(511)
α-Terpineol	(346)
Tetrahydroabietic acid	(470)
Tetrahydroatisine	(267a)
Tetramethylethylene	(360)
dl-Threonine	(525)
Tricyclene	(380)
3,4,5-Trimethyloxazole	(128)
Triolein	(124)
l-Tryptophan	(525)
l-Tyrosine	(525)
Uric acid (potassium salt)	(128)
dl-Valine	(525)
Xanthophyll	(437)

V. Kinetics, Mechanism, and Electronic Interpretation of the Oxidizing Action of Organic Peracids

Most of the discussion in this section will be devoted to the peracid oxidation of olefins, since more study has been devoted to olefins than to any other class of organic compounds oxidized with organic peracids, particularly from the standpoint of reaction kinetics.

The first systematic and reasonably complete interpretation of the reaction of olefinic compounds with organic peracids in the light of modern electronic concepts was recently published by Swern (501). This investigator compiled a list of specific reaction rates (k) for the reaction of aliphatic, alicyclic, and aromatic olefinic compounds with peracetic acid in acetic acid solution and with perbenzoic acid in chloroform or carbon tetrachloride solution. These data, together with additional data, are shown in tables 9, 10, and 11.

TABLE 9

Specific reaction rates (k) for the reaction of aliphatic and alicyclic olefins with peracetic acid in acetic acid solution

OLEFIN	t	$k \times 10^4$*	REFERENCES
	°C.		
Ethylene	25.8	0.19	(114, 115, 499)
Propylene	25.8	4.2	(114, 115, 499)
1-Pentene	25.8	4.3	(114, 115, 499)
1-Pentene	40.9	17.7	(115)
1-Hexene	25.8–26.2	4.9–5.1	(114)
1,5-Hexadiene	25.8	8.0	(115)
1-Heptene	25.8	5.5	(115)
1-Octene	25	5.0	(506)
1-Decene	25	4.7	(506)
Methyl hendecenoate	25	4.1	(217)
2-Methyl-1-propene	25.8	92	(114, 115, 499)
2-Methyl-1-propene	39.9	300	(115)
2-Butene	25.8	93	(115, 499)
2-Pentene	25.8	93–95	(114, 115, 499)
2-Pentene	40.0	309	(115)
2-Hexene	25.8–26.2	99–102	(114, 115, 500)
2-Hexene	41.0	342	(115)
3-Hexene	25.8–26.2	129–134	(114, 115, 500)
3-Hexene	41.0	457	(115)
3-Heptene	25.8	110	(98)
4-Nonene	25.8	105	(98)
Oleic acid	18	36	(111, 487)
Elaidic acid	18	23	(111, 487)
Ricinoleic acid	18	26	(111, 487)
Ricinelaidic acid	18	16	(111, 487)
2-Methyl-2-butene	25.8–26.4	980–1240	(114, 115, 499)
2-Methyl-2-butene	40.8	3000	(115)
Cyclobutene	25.8–26.4	20–22	(114, 115, 500)
Cyclobutene	40.1	60.4	(115)
Cyclopentene	25.8	185–195	(114, 115, 499)
Cyclopentene	39.6	526	(115)
Cyclohexene	15.2	49	(115)
Cyclohexene	25.8	129	(98, 114, 115, 499)
Cyclohexene	39.6	404	(115)
Cycloheptene	25.8	175	(98)
Cycloheptene	39.8	610	(98)
1-Methylcyclopentene	25.8	2220	(114, 115, 499)
1-Methylcyclopentene	40.9	6660	(115)

* Time in minutes; concentration in moles per liter.

On the basis of the electron-releasing and electron-attracting effects of groups attached to or in close proximity to the double bond, and their influence on the nucleophilic properties of the double bond, coupled with the assumption that the peroxide oxygen in organic peracids is electrophilic, a rational explanation was

offered (501) for the marked difference in specific reaction rates of most of the olefinic compounds reported in tables 9, 10, and 11. In addition, explanations were offered for the following facts: (*a*) The reaction of olefins with organic peracids is either slowed down considerably or does not take place at all when carboxyl, carboalkoxy, aldehydo, or keto groups are attached to or are in close proximity to the double bond (75, 431), as is the case in cinnamic (84, 92), sorbic (248, 249, 250), maleic (83, 84), fumaric (84), and crotonic acids (84, 135, 136) and their esters, imidazoledicarboxylic acids (129), allylmalonic acids (103), and 2-pentenoic and 2-hexenoic acids (137); (*b*) aliphatic monoölefins react slowly (217, 499, 500, 506), whereas substitution of the hydrogen atoms attached to the double bond by alkyl groups increases the reaction rate considerably (98, 114, 115, 499, 500), and phenyl groups usually have only a mildly accelerating effect (89, 96, 499); and (*c*) in the oxidation of isoprene, the ethylenic group to which the methyl group is attached is attacked first (86, 438), in the oxidation of

TABLE 10

Specific reaction rates (k) for the reaction of aliphatic and alicyclic olefins with perbenzoic acid

OLEFIN	*t*	$k \times 10^3$*	REFERENCES
	°C.		
Sorbic acid (and alkyl sorbates)	0	0.03–0.05	(249)
Sorbic acid (and alkyl sorbates)	20	0.2	(249)
Sorbamide	0	0.07	(249)
Sorbamide	20	0.45	(249)
Crotonaldehyde	20	0.76	(75)
Sorbyl chloride	0	0.23	(249)
Sorbyl chloride	20	1.52	(249)
Hendecenoic (undecylenic) acid	0	16	(302)
$\Delta^{8,9}$-Menthene-1,2-diol	0	34.7	(346)
Camphene	0	93.1	(346)
Oleic acid	0	384	(302)
Pinene	0	1081	(346)

* Time in minutes; concentration in moles per liter.

2-methyl-2,3-butadiene (a substituted allene), geraniol, linalyl acetate, and citral, the ethylenic group to which two methyl groups are attached is attacked first (86, 431), and in the oxidation of methyl 2,4-hexadienoate (sorbate), the ethylenic group farther from the carbomethoxy group is attacked first (248, 250). Additional information on the influence of substituent groups on specific reaction rates has recently been reported by Heinänen (249).

Performic acid, however, behaves somewhat differently from other organic peracids. This oxidant reacts rapidly with compounds containing one as well as two electron-releasing groups (505, 506), whereas a slow reaction would be expected with the former class of compounds (501).

It is generally accepted that the reaction of organic peracids with olefins is of the second order, although Muskat and Herman (375) have reported that the perbenzoic acid oxidation of the methylstyrylcarbinols is a third-order reaction. Furthermore, the addition of oxygen at the double bond probably takes place

TABLE 11

Specific reaction rates (k) for the reaction of olefins containing aromatic groups with peracetic acid in acetic acid solution and with perbenzoic acid in chloroform or carbon tetrachloride solution

OLEFIN	PERACETIC ACID			PERBENZOIC ACID		
	t	$k \times 10^4$*	References	t	$k \times 10^3$*	References
	°C.			°C.		
Allylbenzene	25.8–26.1	1.9–2.0	(114, 115, 499)	25–30	6–15	(89)
Allylbenzene	39.6	7.4	(115)			
Stilbene	25.8–26.3	5.1–6.7	(114, 115, 499)	0–1	1–2	(89)
Stilbene	39.6	16.7	(115)	15–16	4	(89)
Stilbene				25–30	18	(89)
Isostilbene	25.8	11.1	(115, 499)	0–1	2	(89)
Isostilbene				15–16	9	(89)
Styrene	25.8	11.3	(114, 115, 499)	0–1	2–3.6	(89)
Styrene	40.8	34.4	(115)	15–16	8–25	(89)
Styrene				25–30	35	(89)
1-Phenyl-1-propene	25.8	46	(114, 115, 499)	0–1	3–15	(89)
1-Phenyl-1-propene	40.8	166	(115)	15–16	23–54	(89)
1-Phenyl-1-propene				25–30	110–190	(89)
Indene	25.8	47	(114, 115, 499)			
Indene	41.0	166	(115)			
1,1-Diphenylethylene	25.8	48	(114, 115, 499)			
1,1-Diphenylethylene	39.8	163	(115)			
1,4-Dihydronaphthalene	25.8	37	(114, 115, 499)			
1,4-Dihydronaphthalene	40.9	162	(115)			
1,2-Dihydronaphthalene	16.3	116	(115)			
1,2-Dihydronaphthalene	25.8	230–240	(114, 115, 499)			
1,2-Dihydronaphthalene	40.9	657	(115)			
Triphenylethylene	25.8–26.1	5.76	(114, 115)			
Triphenylethylene	41.2	19.5	(115)			
Methylindene	26.1	599	(115)			
Methylcinnamylideneacetone				0	0.01	(249)
1-Phenyl-2-acetylethylene				20	2.5	(75)
Cinnamic acid (and alkyl cinnamates)				20	0.13	(75)
Cinnamaldehyde				20	4.7	(75)
Cinnamyl alcohol				20	202.5	(75)
1-Phenyl-3-butene				15–16	8–9	(89)
1-Phenyl-2-butene				15–16	10	(89)
1-Phenyl-1-butene				15–16	80	(89)
Eugenol				0	2.2	(346)
Isoeugenol				0	127	(346)
Safrole				0	1.3	(346)
Isosafrole				0	148	(346)
1,1-Diphenyl-1-propene				0	17.7	(346)

* Time in minutes; concentration in moles per liter.

by a *cis*-addition mechanism (24, 135, 296, 502), and the initial product of oxidation is the oxirane compound, which may or may not be the product isolated,

depending on the reaction conditions (217, 501). On hydrolysis of the oxirane ring, with either acids or alkalies, a Walden inversion occurs (309a, 502).

By the application of the principles elaborated by Swern (501), it is possible to predict with a considerable degree of accuracy, especially in the aliphatic series, the specific reaction rate of the peracetic acid oxidation of an olefin of known structure, and suitable and safe reaction conditions can be readily devised. In addition, valuable information regarding the structure of an olefin may be obtained by determining its specific reaction rate with peracids. Also, a determination of the specific reaction rate of a mixture of olefins such as those obtained from dehydration, dehalogenation, dehydrohalogenation, and olefin polymerization reactions yields much information regarding the positions of the double bonds. An analytical method for the determination of "internal" and "external" double bonds in synthetic as well as natural rubbers, based on the rate of reaction of perbenzoic acid with the substance for a definite period of time, and comparison of the quantity of perbenzoic acid consumed with that of known mixtures of model compounds such as oleic and undecylenic acid, has been described by Kolthoff and coworkers (302, 304), Saffer and Johnson (476a), and Weidlein (553).

Only a limited number of kinetic data are available on the oxidation of other types of organic compounds with organic peracids (87, 116, 119, 333, 545), and therefore it is impossible to generalize regarding the mechanism of such oxidations. Furthermore, in some cases the occurrence of secondary reactions has obscured the interpretation of the results. Insofar as reliable information has been accumulated, these oxidations also support the assumption that the peroxide oxygen in organic peracids is electrophilic and is readily released in the presence of nucleophilic substances (501). The observation of Botvinnik (127) that perbenzoic acid reacts with ammonia and amines but not with their salts in which the nitrogen octet is apparently filled is also in line with this assumption.

The electronic structure of organic peracids is not known, but Wittig and coworkers (575, 577, 578) have made some interesting suggestions.

Medvedev and Blokh (345) have determined the rates of reaction of cyclohexene with peracetic, perbenzoic, *p*-methoxyperbenzoic, *m*- and *p*-nitroperbenzoic, and α- and β-pernaphthoic acids in benzene and xylene solutions and have reported that the nature of the solvent affects the speed of the reaction greatly, an observation made earlier by Meerwein and coworkers (346) and Lagrave (311). Kolthoff and coworkers (303) have suggested that chloroform be discouraged as a solvent for perbenzoic acid oxidations because of the high rate of decomposition of the peracid. The addition of 10 per cent of benzene to the chloroform, however, curtails the decomposition.

VI. References[6]

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Addendum[7]

Since December 1, 1947 other references dealing with organic peracids have come to our attention. These are given below in alphabetical order by the first author; the legend in parentheses after the date refers to the section of the present article in which the subject matter of the reference belongs. Of special interest are the papers by Byers and Hickinbottom, who have reported some abnormal reactions in the oxidation of diisobutylenes with organic peracids and are the first workers to have isolated an oxirane compound by the performic acid oxidation of an olefin. The direct perbenzoic acid oxidation of 2-pyridones to hydroxamic acids in 15–20 per cent yield has been reported by Lott and Shaw. Ross, Gebhart, and Gerecht have reported that performic acid oxidation of olefinic compounds having a hydroxyl group on a carbon atom directly adjacent to the olefinic group causes appreciable cleavage of the chain in addition to the expected hydroxylation reaction. Robinson and Waters, and Criegee, have suggested an ionic mechanism for the peracid oxidation of ketones; enolization is *not* the initial step, as had been suggested by Böeseken (82).

[7] Added May 20, 1949.

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