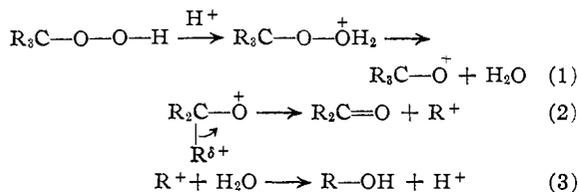Fig. 2.—Effects of acids and bases on oxygen absorption by d-limonene: curve A, 5 ml. of d-limonene plus 1 ml. of water; curve B, 5 ml. of d-limonene plus 1 ml. of 1% citric acid; curve C, 5 ml. of d-limonene plus 1 ml. of 1% sodium carbonate; curve D, 5 ml. of d-limonene plus 1 ml. of 1% phosphoric acid; curve E, 5 ml. of d-limonene plus 1 ml. of 1% sulfuric acid.

virtue of an ionic decomposition of peroxides. Thus, acids may act[4]

$$R_3C\text{—}O\text{—}O\text{—}H \xrightarrow{H^+} R_3C\text{—}O\text{—}\overset{+}{O}H_2 \longrightarrow$$

$$R_3C\text{—}\overset{+}{O} + H_2O \quad (1)$$

$$R_2C\text{—}\overset{+}{\underset{\underset{R^{\delta+}}{|^{\nearrow}}}{O}} \longrightarrow R_2C\text{=}O + R^+ \quad (2)$$

$$R^+ + H_2O \longrightarrow R\text{—}OH + H^+ \quad (3)$$

In the absence of ionic catalysts, hydroperoxides apparently decompose by a free radical mechanism generating new free radicals capable of absorbing oxygen. Such a mechanism accounts for the chain nature of the oxygen absorption process and the autocatalytic effect commonly observed. To the extent that the ionic mechanism pictured above occurs, hydroperoxides are destroyed without the generation of free radicals capable of perpetuating the chains, and the rate of oxygen uptake is diminished. Bases may also catalyze an ionic decomposition of hydroperoxides, perhaps

$$R\text{—}O\text{—}O\text{—}H + OH^- \longrightarrow R\text{—}OH + \bar{O}\text{—}O\text{—}H$$

Experimental[5]

Development of a technique for the measurement of oxygen absorption by d-limonene required a lengthy period of trial and error. Only after many trials was the following procedure worked out: (1) Only rigidly purified d-limonene could be used; the principal offending impurity is the hydroperoxide, which rapidly forms on exposure of d-limonene to air. (2) A rigid cleaning procedure for the reaction

vessel was followed involving degreasing with an organic solvent, boiling in alkaline soap solution for one hour, soaking in potassium dichromate–sulfuric acid cleaning solution for 12 hours, rinsing many times with tap water, rinsing three times with distilled water and finally drying at 150° for at least 12 hours. (3) Fairly rapid shaking of the absorption vessel was necessary; within rather wide limits, however, the rate of shaking seemed not to influence the rate of oxygen absorption. The d-limonene used in all rate experiments was doubly distilled under nitrogen at atmospheric pressure through a 3-foot, helix-packed column and sealed under nitrogen in brown glass bottles. These bottles were stored in the dark until use. The limonene samples were analyzed (see below) for hydroperoxide content immediately before use in a kinetic run. No sample was used if the hydroperoxide content exceeded 0.003 meq./ml.; actually, this figure was seldom approached among the samples used.

The apparatus consisted of a 300-ml. gas buret, jacketed by a water column at room temperature, connected through a three-way stopcock system (necessary for refilling the gas buret) and calcium chloride drying tube to a 125-ml. standard taper erlenmeyer reaction flask through a short piece of capillary tubing sealed through the male joint. The reaction flask was clamped to a shaking arm and vigorously agitated in a constant temperature oil-bath (±0.05°).

A standard procedure was followed in each run. The gas buret was evacuated and filled with oxygen, and the remainder of the system was flushed with oxygen for several minutes. The reaction flask was flushed with oxygen, the components were rapidly pipetted in, and the flask was agitated for five minutes to permit thermal equilibrium before the initial reading of oxygen volume. Readings of oxygen absorption against time were taken until the oxygen absorption reached a maximum and began to fall off. At least two check runs were made of each experiment.

As stated above, a determination of hydroperoxide content was made on each limonene sample prior to use. The method of Wheeler[6] was used with slight modification for these determinations.

(6) D. H. Wheeler, Oil and Soap, 9, 89 (1932).

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Oxidative Ring Enlargement of Cyclic Ketones by Peroxytrifluoroacetic Acid[1]

BY W. F. SAGER AND ALAN DUCKWORTH

Of the many modifications of the ketone oxidation of Baeyer and Villiger there is none that does not suffer from some difficulty sufficiently serious to render the method impractical in certain situations. Caro's acid, besides involving a rather awkward preparation and a somewhat cumbersome work-up due to the heterogeneous nature of the reaction mixture, is unsuitable for the preparation of acid sensitive products such as valero- and caprolactone.[2,3] Alkaline hydrogen peroxide yields the salt of the hydrolyzed product rather than the ester or lactone. Neutral hydrogen peroxide leads to ketone peroxides rather than the cleavage reaction.[4,5] The yields of purified lactones of the type mentioned above obtained by both methods leave much to be desired. The use of hydrogen peroxide in organic acids offers some

(4) Compare M. S. Kharasch, A. Fono and W. Nudenberg, J. Org. Chem., 15, 748 (1950).

(5) Details are here given only for the oxygen absorption studies; readers desiring information regarding the determination of autoxidation products and further detail regarding the oxygen absorption studies should refer to the Ph.D. Dissertation of Samuel E. Horne, Jr., available for loan through the Emory University Library, Emory University, Georgia.

(1) From the M.S. Dissertation of Alan Duckworth, The George Washington University, June, 1954.

(2) R. P. Linstead and H. N. Rydon, J. Chem. Soc., 580 (1933).

(3) R. Robinson and L. H. Smith, ibid., 371 (1937).

(4) M. Stoll and W. Sherrer, Helv. Chim. Acta, 13, 142 (1930).

(5) W. Dilthey, M. Inckel and H. Stephan, J. prakt. Chem., 154, 219 (1940).

TABLE I

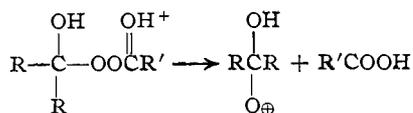| Ketone	Quantity, mole	Yield, %	Found[b]	n^{20}D		Hydrazide, m. p., °C.	
					Lit.	Found	Lit.
Cyclopentanone	0.0964	80.7	1.4613	1.4605[8]			
Cyclopentanone	.0964	88.3	1.4600			114–115	114–115[10]
Cyclohexanone	.1130	76.1	1.4513	1.4568[9]			
Cyclohexanone	.1130	66.6[a]	1.4522			105–106	105–106[11]

(A 5% excess of peracid was used in all experiments) [a] The material balance for this run was considerably below 100%. [b] Calculated from measurements at 25° with a temperature coefficient of 0.0004.

advantages but cannot be compared with the much more effective scheme which employs the peracid itself. Friess has shown that perbenzoic acid is an effective agent for oxidative ring enlargement and gives a reaction mixture which, when purified according to his procedure, yields the desired product easily and in good yield.[6] This method, although the best laboratory procedure reported so far, is capable of improvement in two ways. Perbenzoic acid is prepared by a method which is both tedious and hazardous. In addition, some ketones, especially cyclic ones of large ring size, react slowly. For these reasons we have studied the effectiveness of another peracid in this reaction.

The use of peroxytrifluoroacetic acid was suggested by the recent report of Emmons and Ferris concerning the effortless preparation and remarkable oxidizing properties of this reagent.[7] Theoretical considerations also favor its selection, for if the rate-determining step is that described below, peracids derived from strong acids should react at a greater rate than those derived from weak ones.

$$\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{R-C-OO}}\overset{\overset{OH^{+}}{\|}}{C}R' \longrightarrow \underset{\underset{O\oplus}{|}}{R}\overset{\overset{OH}{|}}{C}R + R'COOH$$

Application of peroxytrifluoroacetic acid to the cleavage of cyclopentanone and cyclohexanone resulted in an almost quantitative reaction which proceeded below room temperature as fast as the reagents were mixed. The product was stable for reasonable periods to the acidic reaction mixture and amenable to ready purification by the procedure of Friess.[5] Three precautions are worthy of mention. Prolonged standing results in formation of a by-product from reaction with trifluoroacetic acid which is probably ω-trifluoroacetoxycaproic acid. Attempts to isolate the lactones by simple distillation caused similar reaction with the acid. Finally, whereas the reaction is not particularly sensitive to water, trifluoroacetic acid may not be used in place of the anhydride for preparation of the peracid for in this case the product is chiefly ketone peroxide.

Experimental

Peroxytrifluoroacetic Acid.—This peracid was prepared by addition of 17.46 ml. (0.6 mole) of 85% hydrogen peroxide to 116.9 g. (0.794 mole) of trifluoroacetic anhydride. This quantity of anhydride is sufficient to react with the water present in the peroxide. One and one-half hours was required for the addition in order to maintain the temperature between 5 and 10°. Actually this procedure was overcautious since the stability of the peracid is such that higher temperatures and hence shorter reaction times can be used without difficulty.

Oxidation Procedure.—The oxidation was carried out in a 250-ml. wide-mouth erlenmeyer flask cooled with an ice-bath and fitted with a thermometer, stirrer and dropping funnel. Cyclic ketone was added to a solution containing a 5% excess of peroxytrifluoroacetic acid in trifluoroacetic acid at such a rate that the temperature remained between 10 and 15°. This usually took about 40 minutes. Titration immediately after completion of the addition revealed a quantity of peracid close to the 5% excess anticipated. The reaction mixture was diluted with 250 ml. of chloroform and poured with cooling and stirring into a quantity of saturated potassium carbonate in excess of that necessary to neutralize the trifluoroacetic acid by 7%. Sufficient water was added to dissolve the precipitated potassium trifluoroacetate, the layers were separated and the aqueous portion extracted once with 100 ml. and twice with 50 ml. of chloroform. The fact that the weight of crude material amounted to 95% of theoretical indicated that very little if any hydrolysis had occurred during the extraction process. The chloroform solution was dried with magnesium sulfate, the solvent removed at room temperature under vacuum, and the product distilled at 2 mm. Results of runs made by this procedure are shown in Table I. Immediate workup is advisable, since a crude product which stood for two days before purification was found to contain between 10 and 20% of acidic by-product, whereas runs purified without delay yielded from 2–5% of this substance. These figures were obtained by titration of samples purified by distillation.

Attempted Purification by Distillation and Other Means.—In an effort to purify by vacuum distillation, the product from 0.106 mole of cyclohexanone and 0.0964 mole of peracid was distilled at 2 mm. until the pot temperature was 150°. After removal of the trifluoroacetic acid, 11.3 g. of acidic product and 2.24 g. of viscous residue were obtained. The fact that the total quantity of material was greater than the theoretical weight of lactone and that the refractive index was very low ($n^{24.5}$D 1.4318) indicates contamination by some substance derived from trifluoroacetic acid, such as trifluoroacetoxycaproic acid. Efforts to remove acidic impurities by neutralization with triethylamine led to sirups which could not be handled successfully. Neutralization with pyridine caused precipitation of such large amounts of solid that filtration was impractical. Ether, as expected, formed an azeotrope with trifluoroacetic acid but purification with its aid offered no advantage over simple distillation.

Effect of Excess Anhydride.—An oxidation carried out with an excess of trifluoroacetic anhydride (0.245 mole of cyclohexanone, 0.25 mole of peracid and 0.003 mole of excess trifluoroacetic anhydride) and which stood for a week before purification gave 18.6 g. of product, b.p. 121° at 1.5 mm., n^{25}D 1.3934. Titration with alkali gave a neutralization equivalent of 114. Moreover, the end-point became fading at the mid-point of the titration and became permanent at the final value listed. Trifluoroacetoxycaproic acid, which would be expected to react with one mole of base instantly and with a second at a measurable rate, has a molecular weight of 228.

Effect of Water.—Cyclohexanone was added to a solution of 0.1 mole of 85% hydrogen peroxide in 0.2 mole of trifluoroacetic acid. The reaction mixture was stirred and kept between 10 and 15°. After about one-half of the theoretical amount of ketone had been added a white precipitate separated. It melted and then flashed when heated on a spatula. The melting point (129.8–130.8°) agreed with the value of 132° reported for the ketone peroxide.[5]

(6) S. L. Friess, THIS JOURNAL, **71**, 2571 (1949).

(7) W. D. Emmons and A. F. Ferris, ibid., **75**, 4623 (1953).

(8) Stoll and Rouvé, Helv. Chim. Acta, **18**, 1087 (1935).

(9) R. P. Linstead and H. N. Rydon, J. Chem. Soc., 580 (1933).

(10) F. J. Van Natta, J. W. Hill and W. H. Carothers, THIS JOURNAL, **56**, 455 (1934).

(11) R. P. Linstead and H. N. Rydon, J. Chem. Soc., 1999 (1934).

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Catalytic Dehydrogenation of Primary and Secondary Alcohols with Platinum and Oxygen: Selective Dehydrogenation in the Steroid Series[1]

BY R. P. A. SNEEDEN AND RICHARD B. TURNER

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Dehydrogenation of primary and of secondary alcohols to aldehydes and ketones, respectively, over metal surfaces at elevated temperature is a well-known and extensively documented procedure.[2] Copper and nickel have been employed most commonly as catalysts in this connection, although the use of silver, ruthenium, platinum, palladium and other elements occasionally has been reported.

In 1855, Strecker[3] noted that cinnamyl alcohol can be converted into cinnamic aldehyde by the action of platinum and oxygen at *room temperature.* Some years later Grimaux[4] observed the conversion of glycerol into glyceraldehyde under similar conditions. The reaction of primary alcohols with platinum and with palladium in the presence of oxygen and of other hydrogen acceptors[5] was studied in greater detail by Wieland, who established that the aldehydes formed initially are subject to further oxidation resulting in the formation of carboxylic acids and of peroxyacids.[6] Despite the obvious potentialities of this procedure, particularly as regards secondary alcohols, applications of the method have been few.[7]

In 1942, Mannich and Siewert[8] attempted catalytic dehydrogenation of the cardiac glycoside, ouabain, and obtained in poor yield two crystalline products, which, however, were incompletely characterized. More recently Heyns and his associates have oxidized successfully a number of sugars to the corresponding sugar acids[9] and have demon-

strated the usefulness of the method in connection with oxidations of inositol[10] and of kojic acid.[11]

Our interest in platinum–oxygen dehydrogenation was aroused by the remarkable selective conversion of the C_3-hydroxyl group of dihydro-ouabagenin into a keto group as described in the preceding paper.[12] We have therefore investigated the action of platinum and oxygen on a variety of other alcohols with a view toward establishing the scope and limitations of the method.

The general procedure adopted in this work was as follows. A suspension of platinum oxide was first reduced to platinum in an atmosphere of hydrogen, and the hydrogen carefully replaced with air by repeated evacuation. The system was then filled with oxygen, and the catalyst suspension was stirred until the uptake of oxygen ceased. A solution of the sample was added through a dropping funnel, and stirring was continued until no further absorption of oxygen was observed. The reaction time in our experiments varied from 7 to about 24 hours. It was subsequently found that air can be substituted for oxygen without any adverse effect upon the reaction rate or upon the yield of oxidation product.

The solvents we have found most satisfactory are ethyl acetate, water, and dilute acetone. Poor yields of impure materials were obtained when acetic acid or dimethylformamide were employed. Our results are listed in Table I. Contrary to the experience of Wieland,[5] we obtained benzaldehyde in good yield by dehydrogenation of benzyl alcohol. In the steroids we have investigated thus far only the C_3-hydroxyl group has proved susceptible to dehydrogenation by this method. The yields obtained are superior to those of partial Oppenauer oxidation,[13–15] and the specificity of

TABLE I

DEHYDROGENATION OF VARIOUS ALCOHOLS WITH PLATINUM AND OXYGEN

No.	Compound	Product	Yield, %
1	n-Octyl alcohol	n-Octyl aldehyde	21[a]
2	Benzyl alcohol	Benzaldehyde	72[a]
3	Cyclohexanol	Cyclohexanone	68[a]
4	2-Methylcyclohexanol	2-Methylcyclohexanone	50
5	Cholestan-3β-ol	Cholestan-3-one	72
6	Cholestan-3α-ol	Cholestan-3-one	50
7	Methyl 3α-hydroxycholanate	Methyl 3-ketocholanate	73
8	Methyl 3α,6α-dihydroxycholanate	Methyl 3-keto-6α-hydroxycholanate	75[b]
9	Methyl 3α,12α-dihydroxycholanate	Methyl 3-keto-12α-hydroxycholanate	70
10	Methyl 3α,7α,12α-trihydroxycholanate	Methyl 3-keto-7α,12α-dihydroxycholanate	70

[a] Isolated as the 2,4-dinitrophenylhydrazone. [b] Isolated as the free acid.

(1) This investigation was supported by a research grant, H-1084, from the National Heart Institute, of the National Institutes of Health, Public Health Service.

(2) J. Houben, "Die Methoden der Organischen Chemie," 3rd. Ed., Vol. II, Georg Thieme, Leipzig (1925), p. 23; A. Mailhe, *Chem. Zeit.*, 29, No. 34, 462 (1905); R. Delaby and J. Dumoulin, *Compt. rend.*, 180, 1277 (1925); R. Delaby, *ibid.*, 182, 140 (1926); W. Triebs and H. Schmidt, *Ber.*, 60, 2335 (1927); A. Halasz, *Ann. Chim.*, 14, 318 (1940); R. Paul, *Bull. soc. chim.*, 5, 1592 (1938); 8, 507 (1941).

(3) A. Strecker, *Ann.*, 93, 370 (1855).

(4) Grimaux, *Bull. soc. chim.*, [2] 45, 481 (1886).

(5) The use of cyclohexanone as a hydrogen acceptor has been shown by E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, 13, 455 (1948), to facilitate nickel-catalyzed dehydrogenations of a variety of secondary alcohols including cholesterol, cholestanol, epicoprostanol, benzhydrol and fluorenol.

(6) H. Wieland, *Ber.*, 45, 484, 2606 (1912); 46, 3327 (1913); 54, 2353 (1921).

(7) In this connection it should be noted that catalytic *oxygenation* of tetrahydrocarbazole over platinum has been employed as a preparative procedure by B. Witkop and J. Patrick, THIS JOURNAL, 73, 2188 (1951).

(8) C. Mannich and G. Siewert, *Ber.*, 75, 750 (1942).

(9) K. Heyns, *Ann.*, 558, 177 (1947); K. Heyns and R. Heinemann, *ibid.*, 558, 187 (1947); K. Heyns and O. Stöckel, *ibid.*, 558, 192 (1947).

(10) K. Heyns and H. Paulsen, *Ber.*, 86, 833 (1953).

(11) K. Heyns and G. Vogelsang, *ibid.*, 87, 13 (1954).

(12) R. P. A. Sneeden and R. B. Turner, THIS JOURNAL, 77, 130 (1955).

(13) J. von Euw, A. Lardon and T. Reichstein, *Helv. Chim. Acta*, 27, 1287 (1944).

(14) T. F. Gallagher and J. R. Xenos, *J. Biol. Chem.*, 165, 365 (1946).

(15) S. Kuwada and S. Morimoto, *Bull. chem. soc., Japan*, 17, 147 (1942).