631. *Catalytic Hydroxylation of Unsaturated Compounds.*

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A systematic examination of various inorganic catalysts for the direct addition of hydrogen peroxide to ethylenic compounds to give glycols (hydroxylation) has been made, using allyl alcohol as the addend and following the course of the reaction by analytical methods. Osmium tetroxide, as is already known, functions well as catalyst; pertungstic acid had now been found to be an efficient catalyst, although it is necessary to carry out the reaction at 50—70° to obtain a reasonable rate. Permolybdic acid and selenium dioxide are rather less efficient, but perchromic and pervanadic acid are very unsatisfactory as they promote undesirable side-reactions. Pertitanic and pertantalic acid have a faint catalytic activity only, and ferrous salts also catalyse the formation of some glycerol. The reaction is most efficiently carried out in aqueous solution in the present case, and where the addend is water-soluble. Examples of the hydroxylation of various other olefinic substances with pertungstic acid as catalyst are described. For the catalytic hydroxylation of olefinic hydrocarbons an organic diluent is necessary to secure interchange between phases; acetic acid is the best diluent which has been examined, and it has been empirically observed that promoting the formation of peracetic acid in the reaction mixture enhances the yield of glycol and rate of reaction, although the underlying reason is not clear.

From present findings and a literature survey, it is shown that, whereas catalysis by osmium tetroxide results in addition of 2 OH in the *cis*-direction, pertungstic acid, pervanadic acid, and selenium dioxide catalyse addition in the *trans*-direction. From this and other facts it is concluded that catalytic hydroxylation is not a homolytic reaction as has been supposed, but heterolytic, and possible reaction mechanisms are discussed.

THE direct conversion of unsaturated compounds into the corresponding αβ-glycols, usually now termed *hydroxylation*, has been known for a considerable time. Leaving out indirect methods, *e.g.*, that through the chlorohydrin, the methods employed may be classified as :

(i) Oxidation by permanganates, chlorates, organic per-acids, etc.

(ii) Direct addition of hydrogen peroxide as such (*a*) in an organic (acetic or formic) acid (Scanlan *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 2305, 2309; 1946, **68**, 1504; Davies, Heilbron, and Owen, *J.*, 1930, 2545; Hilditch, *J.*,1926, 1828) (this reaction undoubtedly proceeds through the per-acid and olefin epoxide), (*b*) in an organic diluent in presence of metallic oxides, or the derived per-acids, capable of acting as H_2O_2-transfer catalysts, and (*c*) under the action of ultra-violet light (Milas, Kurz, and Anslow, *J. Amer. Chem. Soc.*, 1937, **59**, 543).

Methods of Catalytic Hydroxylation.—The present investigation is concerned with an examination of type (ii *b*), that is, direct addition of hydrogen peroxide with inorganic catalysts. The above classification cannot, of course, be taken as rigid, since many inter-connections exist.

The following means of effecting catalytic hydroxylation have previously been described :

(*a*) Catalysis by osmium tetroxide in anhydrous *tert.*-butanol * (Milas *et al.*, *J. Amer. Chem. Soc.*, 1936, **58**, 1302; 1937, **59**, 2345; 1939, **61**, 1845; 1940, **62**, 1841) or other organic solvents (Dupont and Dulou, *Compt. rend.*, 1936, **203**, 92; Coscuig, *Ann. Sci. Univ. Jassy*, Sec. I, 1941, **27**, 303; Clauson-Klaas and Fakstorp, *Acta Chim. Scand.*, 1947, **1**, 216—220; Rosenstein, Canadian P. 440,807).

(*b*) Catalysis by pervanadic or perchromic acid in anhydrous *tert.*-butanol (Milas *et al.*, *J. Amer. Chem Soc.*, 1937, **59**, 2342; B.P. 508,526), or in aqueous methanol or acetone solution (Treibs, *Ber.*, 1939, **72**, *B*, 7; *Brennstoff-Chemie*, 1939, **20**, 358). The patent quoted, and five corresponding U.S. patents, also claim other metallic oxides as catalysts.

(*c*) Catalysis by selenium dioxide in *tert.*-butanol or acetone (Seguin, *Compt. rend.*, 1943, **216**, 667).

According to Treibs (*loc. cit.*), as catalysts are required metal oxides which easily and reversibly form per-acids. Of these he preferred vanadium pentoxide [which forms pervanadic acid, $VO_2(OH)_3$], because molybdenum trioxide and tungsten trioxide, which he considered as possibilities, form per-acids which regenerate hydrogen peroxide only with difficulty. Nothing further has been published concerning the catalytic efficiency of the metallic oxides or per-acids.

Mention might also be made of the use of various metallic ions, such as Fe^{II} and Cu^{II}, to catalyse the oxidising action (*sensu lato*) of hydrogen peroxide (*e.g.*, Fenton, *J.*, 1894, **65**, 899). The oxidising action of Fenton's reagent is inspecific, in fact often destructive, the compound attacked being broken down to formic acid or carbon dioxide. It is now certain that the reagent affords free OH radicals (Waters, *Nature*, 1946, **158**, 380), and the reaction is therefore connected with the catalytic decomposition of hydrogen peroxide (Machu, " Wasserstoffperoxyd u. die Perverbindungen," Vienna, 1937, p. 61; Barb *et al.*, *Nature*, 1949, **163**, 692).

It will be noted that previous workers on catalytic hydroxylation have all worked in organic or aqueous-organic solvents to bring water-insoluble compounds into reaction; little attention seems to have been given to the possibility of working in purely aqueous solution where the solubility of the organic reactant permits this. It is also difficult to find solvents that are unattacked by hydrogen peroxide in presence of catalysts. Treibs (*loc. cit.*) mentions that methanol and acetone are oxidised by hydrogen peroxide in presence of pervanadic acid, but at a rate lower than that of the hydroxylation reaction. Milas used *tert.*-butanol, but we find that although this solvent is indifferent to hydrogen peroxide–osmium tetroxide it is attacked by hydrogen peroxide in presence of pervanadic acid.

It has also been emphasised by most previous workers that working at comparatively low temperatures (*e.g.*, below 20°) is essential in order to keep down side-reactions.

Investigation of Catalytic Activity of Various Metal Per-acids, etc.—A series of experiments was carried out using allyl alcohol as addend, to examine and compare the catalytic activity of various metallic oxides and the derived per-acids. Allyl alcohol has the advantage that both it and its reaction products can be easily determined, and as it is soluble in both water and organic solvents, the effect of these can be studied.

Results of these experiments are summarised in Table I.

(i) *Osmium tetroxide.* Only a few experiments (Nos. 18—21) were carried out with osmium tetroxide, since this is already established as an efficient catalyst. Hydroxylation of allyl alcohol to glycerol by means of hydrogen peroxide in anhydrous *tert.*-butanol took place readily at room temperature in presence of as little as 0·005% w/v of the tetroxide (Expt. 21). It was also established that hydrogen peroxide was stable in *tert.*-butanol solution even in presence of the tetroxide. The anhydrous solvent was however unnecessary, as a theoretical yield of glycerol could be obtained in aqueous solution at room temperature, using a 0·025% concentration of osmium tetroxide, which gave a rapid exothermic reaction (Expt. 19). Formation of acidic by-products was negligible. At 70° the reaction occurred rapidly with only 0·0016% of tetroxide, but the yield was lower.

(ii) *Pervanadic acid.* Numerous experiments were carried out with pervanadic acid as catalyst under various conditions, without good results (Expts. 2—17). Large quantities of

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* This solution of anhydrous H_2O_2 in *tert.*-butanol is often referred to by later authors as *tert.*-butyl hydroperoxide, but this is incorrect. Byers and Hickinbottom (*J.*, 1948, 286) and Gresham and Steadman (*J. Amer. Chem. Soc.*, 1949, **71**, 737), however, have actually used *tert.*-butyl hydroperoxide in *tert.*-butanol for the same reaction. From the work of Milas and Harris (*ibid.*, 1938, **60**, 2434) it would appear that in *tert.*-butanol solution an equilibrium exists between hydrogen peroxide and *tert.*-butyl hydroperoxide.

TABLE I.

Hydroxylation of allyl alcohol under various conditions.

				Starting quantities					Consumption of		Product.			
Expt. no.	Catalyst.	Solvent.	Temp.	H_2O_2, m.-mols.	Allyl alcohol, m.-mols.	Catalyst, mg.	Total vol., ml.	Time for completion.	H_2O_2, m.-mols.	Allyl alcohol, m.-mols.	Glycerol, m.-mols.	Acid, m.-equivs.	% Yield on allyl alcohol consumed.	Remarks.
1	None	H_2O	Room	30·9	35·4	0	6	(19 days)	8·6	5·9	0·6	0·2	10	
2	V_2O_5	,,	,,	114	100	20	50	(21 hr.)	6	—	—	—	—	
3	,,	,,	,,	105	100	100	50	6 days	105	40	10·4	41	26	
4	,,	,,	0°	90	100	100	50	(5 days)	19·9	—	—	—	—	
5	,,	,,	70	91·2	100	20	50	(21·5 hr.)	91·2	87·4	11·6	22·2	13	
6	,,	,,	,,	105	100	50	50	2 hr.	105	81·6	11·7	34·4	11	
7	,,	,,	Room	110	100	20	15	4 days	110	68	8·4	47·5	12	
8	,,	,,	,,	85	100	50	15	18 hr.	83	40	5·0	35·9	12	
9	,,	,,	,,	25	31	25	5	22 hr.	25	15	1·2	10·7	8	
10	,,	,,	,,	110	100	100	15	16 hr.	110	48	17·8	36·2	37	
11	,,	,,	,,	83	100	200	15	0·75 hr.	83	25	11·1	26	45	Cooled to moderate exothermic reaction; 1 m.-equiv. of ester, 2·2 m.-equivs. of CO-compound formed.
12	,,	,,	,,	100·8	100	100	15	23·25 hr.	54	18	1·08	21·8	6	0·5 m.-mol. of H_2SO_4 added.
13	,,	,,	,,	87·9	100	100	15	(6 days)	44	—	—	—	—	Solution kept neutral to phenolphthalein.
14	,,	Dry Bu^{t}OH	,,	95	100	20	60	48 hr.	95	31	6·1	40	20	
15	,,	Aq. Bu^{t}OH	,,	94	100	20	50	2 days	94	34	4·6	41·5	14	41 m.-equivs. of ester formed.
16	,,	Aq. $COMe_2$	,,	31	35	15	16	23 hr.	31	4	1·3	8·6	35	
17	,,	Aq. MeOH	,,	110	100	100	50	22 hr.	108	20	6·0	—	30	
18	OsO_4	H_2O	,,	26	31	0·1	5	2 days	26	25	17·0	1·4	68	
19	,,	,,	,,	110	100	25	50	1 hr.	100	66·6	71·0	0	100	Exothermic.
20	,,	,,	70°	53·5	50	0·4	25	2 hr.	53·5	43·3	24·4	6·9	56	
21	,,	Dry Bu^{t}OH	Room	21·0	20	0·5	10	3·75 hr.	21·0	10·0	6·6	2·1	66	
22	CrO_3	H_2O	,,	85·7	100	20	50	11 days	78·6	32	5·2	1·5	16	Warmed gently to complete reaction.
23	,,	,,	70°	49·6	50	25	25	1·67 hr.	48·8	22·2	8·6	12·1	57	
24	,,	Dry Bu^{t}OH	Room	16·5	20	5	12	6 days	16·1	8	1·8	8·4	22	Warmed gently to complete reaction.
25	TiO_2	H_2O	,,	66	100	20	15	7 days	55	58	7·8	—	13	
26	H_3BO_3	,,	,,	25·6	29·5	50	5	20 days	10·0	7·0	1·1	0·5	16	
27	Fe^{II} NH_4 sulphate $+CuSO_4$	,,	,,	25·6	29·5	{20 20	5	19 days	25·3	20·6	3·9	3·5	16	0·3 m.-mol. of CO-compound formed.
28	SeO_2	,,	,,	26	31	7·5	5	19 days	25	28	11·5	0·7	41	
29	,,	,,	70°	47·0	50	200	25	20·5 hr.	41·2	26·5	17·9	3·2	67	Temp. 100° in last 2 hr.

TABLE I (*continued*).

Expt. no.	Cata-lyst.	Solvent.	Temp.	Starting quantities: H_2O_2, m.-mols.	Allyl alcohol, m.-mols.	Cata-lyst, mg.	Total vol., ml.	Time for com-pletion.	Consumption of: H_2O_2, m.-mols.	Allyl alcohol, m.-mols.	Product: Glycerol, m.-mols.	Acid, m.-equivs.	% Yield on allyl alcohol con-sumed.	Remarks.
30	Ta_2O_5	H_2O	70°	40·4	50	100	50	13 hr.	39·4	30·8	6·7	2·0	17	
31	WO_3	,,	Room	127	100	30	50	17 days	127	100	94	1·5	94	
32	,,	,,	,,	110	100	50	15	14 days	110	91	45	3	49	
33	,,	,,	40°	52·8	50	50	25	10·5 hr.	51·8	46·0	43·0	1·0	94	
34	,,	,,	50	56·9	50	50	25	10·5 hr.	55·8	47·6	43·8	1·0	92	
35	,,	,,	60	53·5	50	50	25	2·5 hr.	53·4	42·6	37·2	1·1	88	
36	,,	,,	70	103·8	100	100	50	2 hr	102·3	82·8	68·2	2·8	83	
37	,,	,,	,,	94·5	100	200	50	1·25 hr.	92·2	83·3	66·1	—	79	In presence of 33 m.-mols. of picric acid.
38	,,	,,	,,	50·7	100	50	25	1 hr.	49·8	38	34·0	0·8	90	
39	,,	,,	,,	102	100	100	18·5	1·3 hr.	100	78	54·2	7·0	70	
40	,,	Aq. Bu^tOH	,,	48·9	50	50	25	9·5 hr.	48·1	31	20·2	—	68	
41	,,	Aq. MeOH	,,	42·4	50	50	25	1 hr.	41·8	6	3·4	0·4	57	3·3 m.-mol. of CO-compound formed.
42	,,	Aq. dioxan	,,	57·2	50	50	25	3 hr.	56·5	24·1	14·9	6·0	62	4·1 m.-mol. of CO-compound formed.
43	,,	Aq. $COMe_2$	,,	54·1	50	50	25	8 hr.	53·1	22·4	19·5	2·6	87	
44	,,	Aq. AcOH	,,	44·7	50	50	25	8·7 hr.	43·5	32·8	15·4	—	47	
45	MoO_3	H_2O	Room	83	100	200	15	25 days	83	89	39·0	3·7	44	
46	,,	,,	70°	45·8	50	200	25	6·5 hr.	45·8	38·0	27·5	4·8	72	

TABLE II.

Hydroxylation of various compounds in aqueous solution with pertungstic acid.

(All experiments conducted at 70°.)

Expt. no.	Olefin hydroxylated.	Starting quantities: H_2O_2, m.-mols.	Olefin, m.-mols.	WO_3, mg.	Total vol., ml.	Time for com-pletion, hr.	Consumption: H_2O_2, m.-mols.	Olefin, m.-mols.	Product: Dihydroxy-compound, m.-mols.	By-products.	% Yield, on olefin con-sumed.	Remarks.
47	Crotonic acid	279	300	150	150	3·7	276	173	Dihydroxybutyric acid, 136·2	Other acid, 15 m.-equivs.	79	See Experimental.
48	Maleic acid	265·8	100	100	50	5·5	259·3	88	Racemic acid, 53·2	HCO_2H, 7·8 m.-mols.	61	See Experimental.
49	K H maleate	200	200	200	100	10·5	200	186	K H racemate, 86	K H oxalate?	45	
50	But-2-en-1-ol	49·8	50	50	25	0·5	49·2	48·9	Butanetriol, 44·5	Acid, 0·5 milli-equiv.	91	See Experimental.
51	Crotonaldehyde	83·1	50	50	25	4	82·3	50·0	Dihydroxybutyric acid, 10·9	Crotonic acid, 13·7 m.-mols.; other acid, 19·0 m.-equivs.	22	
52	4-Vinyl*cyclo*hex-ane-1 : 2-diol	202	100	200	52	7·75	198	55	Dihydroxyethyl-*cyclo*hexanediol, 8·4		15	See Experimental.

acidic by-products were formed, and formic acid was identified in the product, besides small amounts of unidentified carbonyl compounds. The reaction is much slower than with comparable quantities of osmium tetroxide. Further investigation showed that pervanadic acid also catalysed the oxidation of glycerol by hydrogen peroxide at a rate not much slower than that of the hydroxylation reaction, so that the poor yields of glycerol are not surprising. It was also found that in presence of pervanadic acid, hydrogen peroxide rapidly oxidised *tert.*-butanol, methanol, acetone, and dioxan, so that these are inherently unsuitable for use as solvents with this catalyst. Treibs (*loc. cit.*) recommends acetone or methanol as diluents, stating that they are oxidised more slowly than the olefin, but it is clear that attack on the solvent is a serious competitor of the hydroxylation reaction. Milas's recommendation of the same catalyst is actually based on two published experiments (*J. Amer. Chem. Soc.*, 1937, **59**, 2343; a low conversion of benzene into phenol and some oxidative fissions at the double bond by the same reagent are also reported); the numerous results claimed in B.P. 508,526 do not actually specify the catalyst, but are identical as regards products and yields with those elsewhere reported (*J. Amer. Chem. Soc.*, 1936, **58**, 1303; 1937, **59**, 2345) as being obtained by means of osmium tetroxide. It may be concluded that pervanadic acid is not an efficient hydroxylation catalyst.

(iii) *Perchromic acid.* A solution of chromic oxide in hydrogen peroxide (which forms the deep-blue perchromic acid) also proved to be an inefficient hydroxylating agent (Expts. 22—24), either in aqueous or *tert.*-butanolic solution. A further complication is that the catalyst becomes irreversibly reduced to the chromic condition, presumably by the organic reactants, and loses its catalytic power before all the hydrogen peroxide is consumed. The results of Milas (*loc. cit.*) also indicates a low efficiency.

(iv) *Pertungstic acid.* Tungsten trioxide dissolved slowly in 100-volume hydrogen peroxide to give a faintly yellow solution. Aqueous hydrogen peroxide containing catalytic quantities of pertungstic acid reacted extremely slowly with allyl alcohol at room temperature, but eventually efficient conversions (*e.g.*, 94%) into glycerol were obtained (Expt. 31). When a rather larger quantity of catalyst (1·33% w/v concn.) and undiluted 100-vol. hydrogen peroxide were used, the reaction was gently exothermic at first, but several days at room temperature were necessary for complete reaction; the yield in this case was inferior (Expt. 32).

The high efficiency and almost complete absence of by-products obtained by the first procedure then suggested that the reaction might be accelerated by heat without serious loss. This proved to be the case, and the optimum temperature was located at 60—70°, where in aqueous solution approx. 2M. in hydrogen peroxide and containing the equivalent quantity of allyl alcohol and 0·2% w/v of tungsten trioxide the reaction was complete in 2 hours and yields of 80—90% (on allyl alcohol consumed) were obtained. The reaction was further accelerated by an excess of either reagent (Expt. 38), but more concentrated solutions decreased the yield of glycerol at the expense of some acidic by-product (Expt. 39).

Glycerol was not oxidised under the same conditions, and there was no obvious attack by hydrogen peroxide–pertungstic acid on the usual organic solvents; however, use of organic diluents for the reaction gave less successful results (Expts. 40—44). Tungsten trioxide is unfortunately quite insoluble in anhydrous hydrogen peroxide in *tert.*-butanol, but was not precipitated by dilution of its solution in aqueous (30%) hydrogen peroxide with *tert.*-butanol, methanol, dioxan, acetone, or acetic acid. Hydroxylation usually proceeded more slowly at 70° in presence of these diluents than in purely aqueous medium, and loss of peroxide by decomposition (to water and oxygen) was troublesome, especially in methanol; conversions of allyl alcohol were thereby lowered, although the efficiencies were still 47—87%. The question of organic diluents is more fully discussed later in connection with the extension of this method to water-insoluble substances, but the present results indicate that water is the best solvent from the point of view of efficiency of the reaction.

(v) *Permolybdic acid.* Molybdenum trioxide dissolved very slowly in 100-volume hydrogen peroxide. The solution was a fairly efficient hydroxylating agent, but gave an even slower reaction than did pertungstic acid; as in the last case the reaction could be accelerated by raising the temperature to 70°, without increasing side-reactions, but its efficiency was clearly less than that of pertungstic acid (Expts. 45—46).

(vi) *Selenium dioxide.* This functioned slowly but at fair efficiency in aqueous solution; with 0·8% w/v of selenium dioxide, reaction was complete after 18·5 hours at 70° and then 2 hours at 100° (Expt. 29), giving a yield of 67% calculated on the allyl alcohol consumed. Tellurium dioxide is insoluble in water or aqueous hydrogen peroxide, and telluric acid had no catalytic activity.

(vii) *Other catalysts and possible catalysts.* Tantalum pentoxide dissolved in hot 30% hydrogen peroxide only in presence of a trace of alkali, but the solution could then be neutralised without precipitation. Such a solution had a low but definite hydroxylating power (Expt. 30). Pertitanic acid likewise showed a low and inefficient catalytic activity (Expt. 25). Some reaction was observable in presence of boric acid (Expt. 26), but no more than without catalyst (Expt. 1), when the slow reaction was probably photocatalysed. In presence of a little ferrous ammonium sulphate and copper sulphate, allyl alcohol was oxidised slowly by hydrogen peroxide, and glycerol was detected in the product (Expt. 27); hydroxylation by Fenton's reagent does not appear to have been recorded previously but, as is well known, more destructive oxidation is the main reaction, and glycols themselves are also known to be readily attacked by this reagent. Uranium and cerium peroxide are insoluble, no per-acids being formed under the conditions here used; uranyl acetate showed no catalytic activity.

This series of experiments now makes possible an appraisal of the relative merits of various catalysts. Osmium tetroxide maintains its established position as an efficient and powerful catalyst, which does not initiate side-reactions such as destructive oxidation of the product or organic solvent, at any rate at low temperatures. Pertungstic acid is an outstanding new catalyst, which also gives a very high efficiency, but which on account of its lower activity functions best at elevated temperatures and thus differs from most other catalysts. It has, moreover, the advantage over osmium tetroxide of being non-toxic, easier to handle, and readily obtainable in large quantities. Addition of hydrogen peroxide with these two catalysts takes place in different stereochemical directions, as will be discussed more fully below. Pertungstic acid cannot, however, be used in anhydrous solvents and functions best in purely aqueous medium. Permolybdic acid and selenium dioxide are catalysts of low activity but fair efficiency—the observed losses are probably due to the prolonged reaction time. They offer no advantages over the first two catalysts named. Pervanadic and perchromic acid are very unsatisfactory catalysts, as they also catalyse what may be termed " non-specific " oxidation of the product, the organic solvent where used, and quite possibly the starting material as well, so that very large amounts of by-products are formed—in some cases to the total exclusion of glycol. The faint activity of pertitanic and pertantalic acids and the hydroxylating action of Fenton's reagent are of theoretical interest only.

Hydroxylation of Some Other Compounds with Pertungstic Acid in Aqueous Solution (Table II).—A few other water-soluble substances were readily hydroxylated in aqueous solution at 70° in presence of pertungstic acid. Crotonic acid gave 79% (on crotonic acid consumed) of 2 : 3-dihydroxybutyric acid, which from its m. p. (80—81°) was clearly the *erythro*-isomer described by Braun (*J. Amer. Chem. Soc.*, 1929, **51**, 228). Maleic acid, as such, underwent hydroxylation, but much of the hydrogen peroxide decomposed without reacting; the same effect was noticed with crotonic acid and other organic acids, and may be connected with the low pH. By repeated additions of more hydrogen peroxide, all the maleic acid was hydroxylated; the product was identified as racemic acid (Expt. 48). Disodium maleate, on the other hand, caused a rapid decomposition of all the hydrogen peroxide, and only a trace of racemate was formed. Potassium hydrogen maleate, however, was hydroxylated with much better efficiency (based on the hydrogen peroxide) (Expt. 49); the resulting potassium hydrogen racemate crystallised from the solution on cooling, but was contaminated with material of lower acid equivalent (? potassium hydrogen oxalate), from which it could not easily be separated. But-2-en-1-ol was rapidly converted in excellent yield into butane-1 : 2 : 3-triol. Crotonaldehyde reacted readily with aqueous hydrogen peroxide and pertungstic acid at 70°, but detailed analysis showed that oxidation of the aldehyde was competing with hydroxylation. When a further equivalent of hydrogen peroxide was added, in the hope of carrying oxidation through to dihydroxybutyric acid, it became evident that a further side-reaction resulting in the production of other unidentified acids (not formic; possibly oxalic) was occurring (Expt. 51).

Hydroxylation of Olefinic Hydrocarbons with Pertungstic Acid (Table III).—Experiments were made with oct-1-ene and *cyclo*hexene in order to extend the pertungstic acid-catalysed hydroxylation reaction to hydrocarbons. Attempts to carry out the reaction in aqueous suspension were unsuccessful, clearly owing to the mutual insolubility of hydrocarbon and aqueous hydrogen peroxide. Further experiments, in which an organic solvent was used to secure interchange between the two phases, were little more successful. Very poor yields were obtained with *tert.*-butanol, but acetic acid was more promising; an excess of hydrogen peroxide was helpful in acetic acid, and a 45% yield of octane-1 : 2-diol was secured (Expt. 53). Slow addition of the peroxide to the olefin, in an attempt to reduce decomposition, did not improve yields.

TABLE III.

Hydroxylation of hydrocarbons in acetic acid solution with pertungstic acid catalyst (and without catalyst, for comparison).

Expt. no.	Olefin hydroxylated.	Method and temp. (see below).	Starting quantities.			Time, hr.	Consumption of		Product (glycol), m.-mols.	% Yield on olefin consumed.	Remarks.
			H_2O_2, m.-mols.	olefin, m.-mols.	WO_3, mg.		H_2O_2, m.-mols.	olefin, m.-mols.			
53	Oct-1-ene	(A) 70°	166·3	100	200	1·5	163·5	97·6	43·7	45	
54	,,	(B) 70	140	100	200	2·5	127	96·0	77·2	81	
55	,,	(C) 70	194·0	100	200	1	192·5	69·5	59·0	85	
56	,,	(D) 70	200	100	200	46·5	200	93·8	29·5	31	
57	,,	(E) 70	150·4	100	400	2	146·1	79·7	49·8	63	
58	,,	(A) 70	193·6	100	none	19	192·9	95·3	87·2	92	
59	,,	(B) 70	156·2	100	,,	15	155·0	87·5	66·8	76	
60	,,	(C) 70	208·8	100	,,	11·25	207·3	94·2	86·1	91	
61	,,	(E) 70	92·6	100	,,	1	90·2	97·0	37·5	39	
62	,,	(E) 25—50	93·9	100	,,	4·5	90·5	91·4	53·3	55	
63	*cyclo*Hexene	(A) 50	114·8	100	200	10	113·5	97·3	69·2	71	Product is *trans*-diol; see Experimental.
64	,,	(B) 50	128·0	100	200	5	126·2	87·2	64·5	74	
65	,,	(C) 50	122·1	100	200	6·25	119·3	99·4	76·6	77	
66	,,	(A) 50	163·0	100	none	62·5	159·8	98·3	74·1	75	
67	,,	(B) 50	133·5	100	,,	54	130·2	93·7	94·8	101	
68	,,	(C) 50	158·4	100	,,	22·75	156·1	99·7	77·8	78	
69	$CMe_3·CH_2·CMe:CH_2$	(B × 2) 40—65	219	200	200	5·75	211	150	62	41	Other products—see Experimental.
70	$CMe_3·CH:CMe_2$	(B × 2) 40—60	189	200	200	3·25	183	136	122	91	ditto.
71	But-1-ene	(B) 70	169	838	400	9·25	164	822	64	8	See Experimental.
72	$CEt_2:CHMe$	(B × 2) 50—70	200	284	400	3·25	176	277	150	85	ditto.
73	Vinyl*cyclo*hexane	(B) 70	130	50	200	8·25	130	41·8	23·8	57	Yield calc. on assumption that product is tetraol.
74	,,	(B) 70	120·8	100	200	5	116·8	84·3	75·9	90	Yield calc. on assumption that product is diol. See Experimental.

Methods (for details see Experimental): (A) Reactants stirred together in AcOH. (B) H_2O_2–AcOH heated to 80° (1 hr.) before reaction with olefin. (C) Reactants as (A) but with trace of H_2SO_4. (D) H_2O_2–WO_3 added slowly to olefin in AcOH. (E) AcO_2H formed from Ac_2O–H_2O_2–H_2SO_4 and later caused to react with olefin.

Since hydrogen peroxide in acetic acid alone is known to be a hydroxylating agent (see first paragraph), some parallel experiments were made without tungsten trioxide. Reaction thus with oct-1-ene at 70° was extremely slow, but provided that an excess of hydrogen peroxide was initially present, good yields were obtained; *cyclo*hexene was more reactive, and experiments were carried out with this olefin at 50°, although the optimum temperature is undoubtedly higher (Expts. 58, 66). Swern and Scanlan found that reaction is easier if the formation of peracetic acid is facilitated, either by preheating the hydrogen peroxide–acetic acid mixture to 80—85° before causing it to react with the olefin (*J. Amer. Chem. Soc.*, 1940, **62**, 2305), or by adding a little sulphuric acid (*ibid.*, 1945, **67**, 1786). It was found in the present case that some acceleration of the reaction could be secured by these means (Expts. 59, 60, 67, 68).

It was then found that a very substantial increase in rate of reaction, with very good yields, could be brought about by combining either of these two methods of activation with catalysis by pertungstic acid.

Thus, a mixture of 30% hydrogen peroxide (>1 mole) and acetic acid was heated to 80° for 1 hour; the requisite catalytic amount of tungsten trioxide could then be dissolved in this at room temperature (several hours being required for dissolution), after which the solution was mechanically stirred with olefin (1 mole) at a suitable temperature. Reaction was complete in about 2 hours, and yields of 72—91% of diol were obtained (Expts. 54, 64). This method was adopted for several other olefins, and in most cases worked well, although it proved erratic on occasions; it appears that tungsten trioxide, or an impurity in it, catalyses the decomposition of hydrogen peroxide, so that on a few isolated occasions wastage of peroxide occurred.

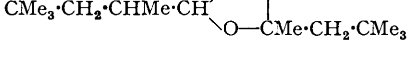
In the other method, the tungsten trioxide was first dissolved in 30% hydrogen peroxide, and this was treated directly with olefin and acetic acid containing a few drops of concentrated sulphuric acid. This procedure was not very fully investigated, but in the case of oct-1-ene and *cyclo*hexene (Expts. 55, 65) was even more successful than the preheating method, 77—85% of diol being obtained. Presumably this method would be unsuitable for olefins sensitive to mineral acid.

The results just described strongly suggested that pertungstic acid also catalyses the addition of peracetic acid to olefins, but experiments in which the per-acid and free hydrogen peroxide were determined by titration during the reaction failed to confirm this; the initial rate of consumption of peracetic acid was little different whether pertungstic acid was present or not, although in the latter case consumption of hydrogen peroxide was very much slower. The two reactions (*a*) pertungstic acid-catalysed reaction between olefin and hydrogen peroxide and (*b*) direct reaction between olefin and peracetic acid, may obviously be superimposed, but reaction (*b*) is very slow compared with (*a*) and would not be expected to affect the results greatly. Possibly in the initial stages of the reaction the peracetic acid, which constitutes some 30% of the total peroxide present, may function as a reservoir of peroxide protected against decomposition. It was also found that in all cases where acetic acid was used as a diluent part of the diol (usually about a half, but the amount was variable) was fixed in a combined state and could only be titrated or isolated after hydrolysis. The nature of the "combined diol" was not investigated, but it was probably an epoxide and/or acetate.

A few other variations in procedure were tried, without success (Expts. 56, 57, 61, and 62).

The "preheating" method was applied to both isomers of di*iso*butylene, which reacted easily thus. The reaction was complicated here by the appearance of by-products similar to those observed by Byers and Hickinbottom (*J.*, 1948, 268, 1328). 2 : 4 : 4-Trimethylpent-1-ene gave only a 41% yield of diol (by titration), and a little 4 : 4-dimethylpentan-2-one (isolated as 2 : 4-dinitrophenylhydrazone) was found amongst the products, as also observed by Byers and Hickinbottom and possibly arising from oxidation of the diol. A high-boiling by-product, probably identical with that obtained by Byers and Hickinbottom and presumed by them to be 2 : 4-dimethyl-2 : 4-di*neo*pentyldioxan, was in the present case characterised, by its identity (infra-red absorption spectrum) with a synthetic sample, as the cyclic acetal between the diol and 2 : 4 : 4-trimethylpentanal, *i.e.*, *4-methyl-4-*neo*pentyl-2-(4′ : 4′-dimethyl-2′-pentyl)dihydrodioxole* (I). 2 : 4 : 4-Trimethylpent-2-ene gave 91% of titrated diol, but the amount actually isolated was much less than this, and here again high-boiling by-products

(I.)



were obtained. Byers and Hickinbottom (*ibid.*, p. **1331**) traced formation of these by-products in their case (*i.e.*, using peracetic acid alone) to irregular hydrolysis of the epoxides, which here are the precursors of the respective diols. Formation of very similar by-products in the present instance points to the epoxide being an intermediate also in the catalytic hydroxylation (see below).

In order to see if the branched >C:C· structure was reponsible for such irregularities, 3-ethylpent-2-ene (from triethylcarbinol) was submitted to reaction under the same conditions, but it gave an 85% yield of diol and no obvious by-products beyond a trace of ketonic material. Incidentally, mesityl oxide failed to undergo hydroxylation (or epoxidation) with any of the procedures here described.

But-1-ene was passed, as gas, into the reagent at 70°; reaction was fairly rapid at first, but later became very slow, and a good deal of butene was wasted in forcing the consumption of peroxide to completion. Butane-1 : 2-diol was obtained, but the reaction would evidently be more satisfactorily carried out under pressure.

4-Vinyl*cyclo*hexene was readily hydroxylated as far as *4-vinyl*cyclo*hexane-1 : 2-diol;* hydroxylation of the second double bond could be carried out either thence, or directly from the diene by the use of two molar equivalents of hydrogen peroxide, to given an intractable substance presumed to be the saturated tetraol (4-1′ : 2′-dihydroxyethyl*cyclo*hexane-1 : 2-diol). The hydroxylation of vinyl*cyclo*hexene and characterisation of the product have been further studied by Mr. L. S. Abbott of this Department (Abbott and Faulkner, to be published).

The product from *cyclo*hexene proved to be *trans-cyclo*hexane-1 : 2-diol. Hydroxylation with osmium tetroxide in *tert.*-butanol was found by Milas and Sussman (*J. Amer. Chem. Soc.*, 1936, **58**, 1302) to give the *cis*-diol, and this we are able to confirm; Dupont and Dulou (*Compt. rend.*, 1936, **203**, 92) state that the product is mixed *cis*- and *trans*-diols, but this assertion appears to be based on the low melting point of their product, and no separation of isomers is reported. The formation of different isomers by different catalysts leads to the more general question of the stereochemistry of addition of hydrogen peroxide under different conditions.

Stereochemistry of Catalytic Hydroxylation.—Milas and Sussman (*J. Amer. Chem. Soc.*, 1937, **59**, 2345) were of the opinion that, in all catalytic hydroxylations, addition of 2 OH took place in the *cis*-direction. Whereas Milas's own results do in fact show that, in all cases where two isomers arise and are identifiable, hydroxylation with osmium tetroxide gives only *cis*-addition, his papers carry no concrete evidence for extending this to other catalysts. Treibs (*Angew. Chem.*, 1939, 698) states, on the other hand, that addition of hydrogen peroxide in presence of pervanadic acid always proceeds in the *trans*-direction, but he quotes experimental evidence only for *cyclo*hexene. A survey of the direction of addition in all reported cases is given in Table IV.

TABLE IV.

Addition to :	Catalyst.	Product.	Direction of addition.	Ref.
*cyclo*Hexene	OsO_4	*cis*-Diol	*cis*	[1, 4]
,,	,,	*cis* + *trans*-Diol *	both	[6]
2 : 4-Dimethyl-5 : 6-dihydropyran	,,	*cis*-Diol	*cis*	[9]
Maleic acid (*cis*-)	,,	*meso*Tartaric acid *	*cis*	[2]
Fumaric acid (*trans*-)	,,	Racemic acid *	*cis*	[2]
Et_2 maleate (*cis*-)	,,	Et_2 *meso*tartrate	*cis*	[5]
Et_2 fumarate (*trans*-)	,,	Et_2 racemate	*cis*	[5]
Oleic acid (*cis*-)	,,	*erythro*-Dihydroxystearic acid [10]	*cis*	[5]
Cinnamyl alcohol (*trans*-)	,,	*threo*-Stycerol	*cis*	[5]
*cyclo*Hexene	SeO_2	*trans*-Diol	*trans*	[7]
,,	Pervanadic acid	,,	*trans*	[8]
Et_2 fumarate	,,	Racemic acid *	*cis*	[3]
*cyclo*Hexene	Pertungstic acid	*trans*-Diol	*trans*	[1]
Maleic acid (*cis*-)	,,	Racemic acid	*trans*	[1]
Crotonic acid (*trans*-)	,,	*erythro*-Dihydroxybutyric acid	*trans*	[1]

* In these cases the product was not unequivocally identified as such.

[1] Present work. [2] Milas *et al.*, *J. Amer. Chem. Soc.*, 1936, **58**, 1302. [3] *Idem, ibid.*, 1937, **59**, 2342. [4] *Idem, ibid.*, p. 2345. [5] *Idem, ibid.*, 1939, **61**, 1844. [6] Dupont and Dulou, *loc. cit.* [7] Seguin, *loc. cit.* [8] Treibs, *Angew. Chem.*, 1939, 698. [9] Gresham and Steadman, *J. Amer. Chem. Soc.*, 1949, **71**, 737. [10] See Wittcoff and Miller, *ibid.*, 1947, **69**, 3138.

It is at once evident that, neglecting doubtful cases, the hydroxyl groups are added in the *cis*-direction by osmium tetroxide catalysis, and that with selenium dioxide, pervanadic and pertungstic acid addition is *trans* for all cases so far recorded.

Organic per-acids in general are well known to be reagents for *trans*-addition of two hydroxyl groups, but here the epoxide is an isolable intermediate.

Mechanism of Catalytic Hydroxylation.—Up to the present, hydroxylation with inorganic catalysts has been held to involve the liberation of free hydroxyl radicals, followed by attack by these upon the ethylenic linkage (Milas *et al.*, *locc. cit.*; Waters, *Ann. Reports*, 1945, **42**, 146, and " Chemistry of Free Radicals," Oxford 1944, p. 246). On the experimental evidence now available, this view cannot be maintained. First of all, the complete difference in stereochemical sense of addition in presence of osmium tetroxide and of the other catalysts demonstrates a fundamental difference in mechanism between the two types of catalyst. Waters (*loc. cit.*, 1946) has already foreshadowed such a difference, since an alternative explanation for the action of osmium tetroxide lies in the formation of a cyclic osmic ester followed by oxidative hydrolysis, and in fact these two steps are separately realisable (Criegee, *Annalen*, 1936, **522**, 75). The experimental facts are rather strongly in favour of such a mechanism.

There remains the group of *trans*-hydroxylating catalysts. Here again there is little *a priori* evidence for a free-radical mechanism. The clean reaction in concentrated solution and exclusive product of only one stereoisomer, obtained with pertungstic acid catalysis, speak, indeed, in favour of an ionic mechanism (the same remarks may be applied to the osmium tetroxide reaction). Although a few homolytic reactions giving good yields of a single product are known, the majority give a number of products, or, from the preparative point of view, a preponderance of side-reactions. Homolytic fission of the hydrogen peroxide molecule into two hydroxyl radicals under the influence of a metallic ion, as implied by Milas, does not in fact appear to have been observed experimentally; the normal mechanism of liberation of hydroxyl radicals by metallic ions is believed to be on the lines :

$$\mathrm{M} + \mathrm{H_2O_2} \longrightarrow \mathrm{M^+} + \mathrm{OH^-} + {\cdot}\mathrm{OH}$$

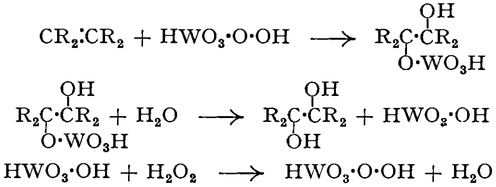
giving not more than one hydroxyl radical per molecule of hydrogen peroxide decomposed (see, *e.g.*, Barb *et al.*, *loc. cit.*). The catalytic hydroxylation reaction may be contrasted with the action of lead tetra-acetate on olefins whereby glycol diacetates are obtained :

$$\mathrm{CR_2{:}CR_2} + \mathrm{Pb(OAc)_4} \longrightarrow \mathrm{AcO{\cdot}CR_2{\cdot}CR_2{\cdot}OAc} + \mathrm{Pb(OAc)_2}$$

Although formally analogous to hydroxylation, this clearly involves the addition of free acetoxyl radicals, and not only does addition frequently take place in both *cis*- and *trans*-directions, but substitution of hydrogen atoms by acetoxyl is at least as important as addition to the double bond (Criegee, *Annalen*, 1930, **481**, 263). Incidentally, Milas, Kurz, and Anslow (*loc. cit.*) do not provide evidence for the stereochemical direction of addition of hydrogen peroxide under the influence of ultra-violet radiation, but the fact that the dihydroxybutyric acid they obtained from crotonic acid was not crystalline strongly suggests that it was a mixture of isomers. It is noteworthy that half the peroxide consumed in this process was decomposed to oxygen and water.

Further evidence against the participation of free radicals in the catalytic reaction was afforded by the observation that it is quite uninhibited by picric acid (Expt. 37), which is known to terminate free-radical reaction chains by combination with the active radicals.

Interaction of olefins with organic per-acids leads to *trans*-diols. However, the mechanism is here clear, at least in the later stages, since epoxides are known intermediate products and these on ring fission, involving a Walden inversion at one carbon atom, give *trans*-diols. It is possible, and even probable, that reaction of an olefin with pertungstic acid ($\mathrm{HWO_3{\cdot}O{\cdot}OH}$), which is formally analogous to peracetic acid, may also give the epoxide; the apparent impossibility of using pertungstic acid in anhydrous solvents prevents a direct proof of this. The mechanism by which the epoxide is formed from olefin and organic per-acids is, however, still unknown. The reaction is facilitated by increased nucleophilic character of the double bond, and is considered by Swern (*J. Amer. Chem. Soc.*, 1947, **69**, 1692) to be an ionic addition reaction. One may deduce that the first step is addition of a cation (either free or " potential ") to the electronegative side of the double bond. Swern (*loc. cit.*) assumes that this cation is $\mathrm{O^+}$, admitting ignorance of how this might actually be liberated from the per-acid. More probably it is an oxygen-containing cation, possibly arising from polarisation of the per-acid in the sense $\overset{-}{\mathrm{O}}\mathrm{Ac{\cdot}}\overset{+}{\mathrm{O}}\mathrm{H}$ (cf. Criegee, *Annalen*, 1948, **560**, 131). A similar postulate could be applied to the case of pertungstic acid if this could react as $H\overset{-}{W}O_4{\cdot}\overset{+}{O}H$; a qualitative increase in reactivity with nucleophilic character of the double bond can be discerned in the present instance also. It is actually unnecessary to postulate intermediate formation of the epoxide in this case, since ionic addition is normally *trans*; the reaction could be



$$CR_2{:}CR_2 + HWO_3{\cdot}O{\cdot}OH \longrightarrow R_2\underset{O\cdot WO_3H}{\overset{OH}{C}}{\cdot}CR_2$$

$$R_2\underset{O\cdot WO_3H}{\overset{OH}{C}}{\cdot}CR_2 + H_2O \longrightarrow R_2\underset{OH}{\overset{OH}{C}}{\cdot}CR_2 + HWO_3{\cdot}OH$$

$$HWO_3{\cdot}OH + H_2O_2 \longrightarrow HWO_3{\cdot}O{\cdot}OH + H_2O$$

Since hydrogen peroxide has very little tendency to react as $\overset{+}{O}H\ \overset{-}{O}H$, it naturally cannot readily add directly to an ethylenic linkage without the mediation of a catalyst.

It may also be seen that a gradation exists from catalysts such as pertungstic acid, which is almost exclusively hydroxylating, through those such as pervanadic acid which give much "non-specific" oxidation as well, to those such as ferrous salts which result almost invariably in "non-specific" oxidation to a variety of products, often as far as carbon dioxide. Since the last type of behaviour is ascribed to liberation of free hydroxyl radicals, it is reasonable to suppose that catalysts of the type of pervanadic acid may indeed also give rise to hydroxyl radicals, but that these are responsible, not for the hydroxylating action, but for the observed side-reactions.

EXPERIMENTAL.

Quantitative work.

Methods of Analysis.—Hydrogen peroxide was determined iodometrically by the procedure of Kolthoff and Sandell ("Textbook of Quantitative Inorganic Analysis," Macmillan 1943, p. 630). In experiments involving acetic acid, it was sometimes of interest to titrate hydrogen peroxide and peracetic acid separately, which was done by the method of Smit (*Rec. Trav. chim.*, 1930, **49**, 675).

Olefins were determined by the bromide–bromate procedure where applicable. For hydrocarbons and maleic acid the modified method of Lucas and Pressman (*Ind. Eng. Chem. Anal.*, 1938, **10**, 140) was used.

Glycols were determined by a modification of the method of Vorhees, Ellis, and Maynard (*J. Biol. Chem.*, 1940, **133**, 491) which has been developed in the Analytical Section of this Department. The sample ($<$0·4 millimol. of glycol) is added to 50 ml. of a reagent, containing 2·5 g. of potassium iodate and 10 g. of magnesium sulphate heptahydrate in 1 l. of 0·1N-sulphuric acid. After ½ hour the solution is diluted to about 150 ml., and N-NaOH added until a permanent turbidity appears, followed by 10 ml. of buffer solution (120 g. of $Na_2HPO_4,12H_2O$ and 35 ml. of 10N-H_2SO_4 in 1 l., adjusted to pH 4) and 10 ml. of 10% potassium iodide. The liberated iodine is then titrated (slowly) with 0·1N-sodium thiosulphate.

Hydrogen peroxide, when present, interferes with the determination of both olefins and glycols, and was conveniently removed by neutralising the mixture, then adding equivalent amounts (about 0·5 milliequiv.) of sodium hydroxide and silver nitrate, and boiling the solution for 5 minutes. In experiments in acetic acid solution, about half the glycol was "free" and the remainder "combined" (presumably as ester or epoxide) and only titratable after boiling the sample for 1 hour with an excess of 2N-sodium hydroxide.

Ketones were determined by means of an alcoholic hydroxylamine hydrochloride reagent (Maltby and Primavesi, *Analyst*, 1949, **74**, 498). Acids were titrated conventionally.

Materials.—Vanadium pentoxide was of reagent grade; a few experiments were made in which it was purified by conversion into the sulphide and ignition, followed by dissolution in hydrogen peroxide and reprecipitation by boiling the solution. No difference in catalytic properties was found in the purified material.

Tungsten trioxide was a commercial sample. After long storage in a clear glass bottle, it formed some dark lower oxide which was not only insoluble in hydrogen peroxide but catalysed the decomposition of the latter. Trioxide stored in the dark did not deteriorate thus.

Hydrogen peroxide was commercial "100-volume," and presumably contained stabilisers.

Most of the allyl alcohol used was "Kahlbaum's pure" in sealed ampoules. A sample from B.D.H. Ltd. was fractionated through a column before use and had b. p. 97—98°.

Other olefins were either fractionated commercial samples or prepared in these laboratories.

Methods.—In general, the experiments consisted in allowing olefin, hydrogen peroxide, catalyst, and diluent to react at room temperature or immersed in a thermostatically controlled heating bath, following the progress of the reaction and finally determining the products by titrating suitable aliquots for hydrogen peroxide, olefin, glycol, and by-products where appropriate. In cases where the reaction mixture was not homogeneous, it was mechanically stirred so as to obtain thorough emulsification, and experiments at elevated temperatures were conducted under reflux. Details of the quantities and conditions employed and results obtained are summarised in Tables I—III. It will be noted that in most cases some unchanged olefin remained, and that yields are calculated on the olefin consumed. Some further experimental details of typical experiments will be found below, under "Products"

Runs in aqueous solution were carried out by dissolving the catalyst in 30% hydrogen peroxide diluting the solution somewhat with water, adding the olefin to be hydroxylated, and diluting the mixture finally to the required volume, usually bringing the hydrogen peroxide concentration to about **2M.** In some experiments (Nos. 1, 7—13, 18, 25—28, 32, 45) no diluent was added.

Anhydrous hydrogen peroxide in *tert.*-butanol was prepared by the method of Milas (*loc. cit.*), except that anhydrous magnesium sulphate was found a better dehydrating agent than sodium sulphate.

The following procedures were used in attempts to hydroxylate olefinic hydrocarbons (Table III); the preferred methods are B and C.

Method A. 30% Hydrogen peroxide (14·25 ml.), containing tungsten trioxide (0·2 g. where used), was stirred mechanically at the stated temperature with 45 ml. of glacial acetic acid and 0·1 ml. of hydrocarbon.

Method B. A mixture of 30% hydrogen peroxide (14·25 ml.) and glacial acetic acid (45 ml.) was heated to 80° for 1 hour; the tungsten trioxide (0·2 g., where used) could then be dissolved in this by setting the mixture aside for several hours at room temperature, and the prepared solution was then stirred with hydrocarbon (0·1 mol.) at the stated temperature.

Method C. As A, but with the prior addition of 2 drops of concentrated sulphuric acid.

Method D. 30% Hydrogen peroxide (15 ml.) containing tungsten trioxide (0·2 g.) was added slowly during the time stated to a stirred, heated mixture of hydrocarbon (0·1 mol.) in acetic acid (35 ml.).

Method E. Tungsten trioxide (0·2 g., where used) was dissolved in 30% hydrogen peroxide (20 ml.) and kept at 21—24° for 4 hours with acetic anhydride (100 ml.) and concentrated sulphuric acid (1 g.). The sulphuric acid was neutralised by the addition of anhydrous sodium acetate (2·5 g.), and the decanted solution was then stirred with hydrocarbon at the temperature stated.

Products.

Arising from the experiments herein described, hydroxylation products were isolated from the following starting materials:

Allyl Alcohol (Table I).—The products from a number of runs were pooled, and, after evaporation of water and unchanged allyl alcohol, distillation afforded glycerol, b. p. 180°/15 mm. (tribenzoate, m. p. 69·5°).

But-2-*en*-1-*ol* (Expt. 50).—Hydroxylation of but-2-en-1-ol in aqueous solution with pertungstic acid gave butane-1 : 2 : 3-triol, b. p. 170°/20 mm., n_D^{20} 1·4622 (Lieben and Zeisel, *Monatsh.*, 1880, **1**, 832, give b. p. 172—175°/27 mm.).

Crotonic Acid (Expt. 47).—From the hydroxylation product, unchanged crotonic acid was extracted with chloroform, and the aqueous layer on evaporation yielded *erythro*-1 : 2-dihydroxybutyric acid, m. p. 82—83° (from ethyl acetate) (Braun, *J. Amer. Chem. Soc.*, 1929, **51**, 228, gives m. p. 81·5°, the *threo*-isomer having m. p. 75°).

Maleic Acid (Expt. 48).—The hydroxylation of maleic acid was forced to substantial completion by addition of further quantities of hydrogen peroxide. On evaporation to dryness, a 61% yield of racemic acid, m. p. 203—204° (from acetone), was obtained. After reaction of potassium hydrogen maleate with hydrogen peroxide and pertungstic acid (Expt. 49), the aqueous solution crystallised on cooling. The isolated crystals gave a low titration equivalent for potassium hydrogen racemate, and contained a tenaciously-held impurity (potassium hydrogen oxalate ?); some pure racemate (Found: equiv., 187. Calc. for $C_4H_5O_6K$: equiv., 188) was, however, obtained after lengthy fractional crystallisation.

Oct-1-*ene* (Expts. 53—62).—Octene was hydroxylated by method B or C (see above), and some solvent removed from the product under reduced pressure. The residue was heated under reflux for 1 hour with an excess of aqueous sodium hydroxide (about 2N.), and the glycol extracted with ether. It had m. p. *ca.* 25°, b. p. 137—139°/20 mm. (Swern, Billen, and Scanlan, *J. Amer. Chem. Soc.*, 1946, **68**, 1504, found m. p. 30—35°, b. p. 135—136°/10 mm.), and yielded a *di*-1-*naphthylurethane*, m. p. 112—114° (from light petroleum) (Found: N, 5·5. $C_{30}H_{32}O_4N_2$ requires N, 5·9%).

cyclo*Hexene* (Expts. 63—68).—By similar means (except that continuous extraction of the product with ether was required), *cyclo*hexene yielded *trans*-*cyclo*hexane-1 : 2-diol, b. p. 130—140°/30 mm., m. p. 102° (from ethyl acetate) (dibenzoate, m. p. 91—92°). Hydroxylation of *cyclo*hexene (100 millimols.) by anhydrous hydrogen peroxide (101·6 millimols.) in *tert.*-butanol at 20° with osmium tetroxide (15 mg.) as catalyst, following the general directions of Milas (*loc. cit.*), gave 47% (by titration; calc. on *cyclo*hexene consumed) of *cis*-*cyclo*hexane-1 : 2-diol, b. p. 120—140°/15 mm., m. p. 95—96° (from ethyl acetate) (dibenzoate, m. p. 63—65°). Rothstein (*Ann. Chim.*, 1930, **14**, 461) gives: *trans*-diol, m. p. 104°, b. p. 117°/13 mm. (dibenzoate, m. p. 92°); *cis*-diol, m. p. 98°, b. p. 116°/13 mm. (dibenzoate, m. p. 63·5°; the m. p. of 71·5° reported by Brunel, *Compt. rend.*, 1903, **136**, 384, appears to be erroneous).*

2 : 4 : 4-*Trimethylpent*-1-*ene* (Expt. 69).—This (100% pure; n_D^{18} 1·4136) was hydroxylated by method B. The hydrolysed product from 22·4 g. of olefin was distilled through a semi-micro-column (3 theoretical plates), and the fractions, after removal of solid glycol, were further separated in a micro-column. The following cuts were finally obtained:

	B. p.	n_D^{18}.	Weight, g.
(i)	100—106°	1·4095	5
(ii)	105—125°	1·4119	1
(iii)	126—128°	1·4110	1
(iv)	167—163°	1·4146	1
(v)	90—108°/15 mm.	1·4398	0·22
(vi)	112—116°/15 mm.	1·4421	1·18
(vii)	216—220°	(solid)	1·90
(viii)	130—132°/15 mm.	1·4430	1·71
(ix)	145—146°/15 mm.	1·4441	1·06

Fraction (vii) after recrystallisation from light petroleum gave 2 : 4 : 4-trimethylpentane-1 : 2-diol prisms, m. p. 59° (Prileschajew, *Ber.*, 1909, **42**, 4811, gives m. p. 60—61°). Fraction (iv) may be

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* Mixed *cis*- + *trans*-*cyclo*hexane-1 : 2-diol is conveniently prepared by hydrogenation of *cyclo*hexan-1-ol-2-one, which may be obtained through chlorination of *cyclo*hexanone (Young, B.P. 576,680).

the corresponding unsaturated alcohol, as observed by Byers and Hickinbottom (*J.*, 1948, 1328, 1331). Fraction (iii) proved to be 4 : 4-dimethylpentan-2-one identified by the 2 : 4-*dinitrophenylhydrazone*, yellow needles, m. p. 90—92° (Found : C, 52·8; H, 6·0. $C_{13}H_{18}O_4N_4$ requires C, 53·0; H, 6·2%). An authentic specimen of (III) (semicarbazone, m. p. 174—175°; lit., 176°), obtained by the method of Byers and Hickinbottom (*ibid.*, p. 1336), gave the same hydrazone, m. p. 94—95° (no depression of mixed m. p.). Whitmore *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 2035) record m. p. 100°, but did not analyse their derivative.

The higher fractions with 2 : 4-dinitrophenylhydrazone in 2N-hydrochloric acid gave a yellow hydrazone, m. p. 140—141°, probably that of 2 : 4 : 4-trimethylpentanal (lit., m. p. 145°) (Found : C, 54·1; H, 6·1. Calc. for $C_{14}H_{20}O_4N_4$: C, 54·5; H, 6·5%).

Fraction (ix) contained a little active hydrogen (Found : 0·058%), but examination of its infra-red absorption spectrum demonstrated it to be mainly 4-*methyl*-4-neo*pentyl*-2-4′ : 4′-*dimethyl*-2′-*pentyl-dihydrodioxole* (I). A synthetic sample of (I) was prepared by heating equivalent quantities of (II) and (IV) in benzene with a few drops of concentrated hydrochloric acid in a Dean–Stark apparatus until water ceased to be evolved. Distillation gave (IV), b. p. 130°/12 mm., n_D^{20} 1·4412 (Found : C, 74·5; H, 13·0. $C_{16}H_{32}O_2$ requires C, 75·0; H, 12·5%). The infra-red absorption spectrum was compared with that of fraction (ix) above by Mr. A. R. Philpotts of this Department, who reported that they were almost identical, both having a characteristic series of bands of the same relative intensities at 905, 926, 957, 982, 1002, 1016, 1038, 1065, 1086, 1100, 1208, and 1254 cm.$^{-1}$, the last two bands being attributed to *tert.*-butyl groups. Fraction (ix) in addition gave some evidence of impurity, which is not surprising. Byers and Hickinbottom (*loc. cit.*, p. 1329) record b. p. 128°/19 mm., n_D^{20} 1·4412, for the compound described by them as 2 : 5-dimethyl-2 : 5-di*neo*pentyldioxan.

2 : 4 : 4-*Trimethylpent*-2-*ene*.—This isomer (96·5% pure; n_D^{18} 1·4130) was hydroxylated in better yield but still gave a large range of by-products. Fractionation of the product from 22·4 g. of olefin finally gave :

	B. p.	n_D^{18}.	Weight, g.		B. p.	n_D^{18}.	Weight, g.
(i)	101—107°	1·4140	4·5	(v)	95—108°/15 mm.	(pasty)	0·5
(ii)	117—154°	1·4802	0·5	(vi)	198—200°	(solid)	2·6
(iii)	154—165°	1·4134	0·3	(vii)	124—140°/15 mm.	1·4480	0·2
(iv)	180—185°, 76— 95°/15 mm.	1·4336	1	(viii)	148—150°/15 mm.	1·4505	1

Fraction (vi) was 2 : 4 : 4-trimethylpentane-2 : 3-diol, and after recrystalisation from light petroleum formed needles, m. p. 65° (Prileschajew, *loc. cit.*, records m. p. 65—66°). All these fractions gave precipitates of unsharp m. p. with 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid; fractional crystallisation yielded a reddish-orange derivative, m. p. 200—202°, probably the pyrazoline described by Byers and Hickinbottom (*loc. cit.*, p. 284) (Found : C, 54·5; H, 6·5. Calc. for $C_{14}H_{18}O_4N_4$: C, 54·9; H, 5·9%), and a more soluble hydrazone which could not be purified beyond m. p. 95—125°. Fraction (viii) contained 0·27% of active hydrogen (Calc. for $C_{16}H_{31}O_2{\cdot}OH$: 0·37%), and may well have been a mixture of dioxan derivatives of the type described by Byers and Hickinbottom.

Commercial di*iso*butylene gave, as expected, a mixture of the products from the two isomers. The diols were separable by fractional distillation.

3-*Ethylpent*-2-*ene* (Expt. 72).—The olefin, b. p. 85—88°, n_D^{15} 1·4142, was obtained by distilling 3-ethylpentan-3-ol (Davies and Kipping, *J.*, 1911, **99**, 298) with sodium hydrogen sulphate. The product (method B) was fractionated in a search for by-products, giving : (i) b. p. <100°, 1·4 g.; (ii) b. p. 105—183°, 1·4 g.; and (iii) b. p. 200—201°, 7·0 g., n_D^{20} 1·4464. Fraction (iii) was 3-ethylpentane-2 : 3-diol (Tiffeneau and Dorlemont, *Compt. rend.*, 1906, **143**, 127, give b. p. 194—197°). Fraction (ii) gave in small yield a 2 : 4-dinitrophenylhydrazone, m. p. (incomplete) 133°, and evidently contained but small amounts of any individual ketone.

But-1-*ene* (Expt. 71).—Saturation of the reagent of method B with but-1-ene and working up in the usual way resulted in butane-1 : 2-diol, b. p. 96°/16 mm., n_D^{20} 1·4337 (Tischchenko and Churbakov, *J. Gen. Chem. Russia*, 1937, **7**, 663, give b. p. 191°, n_D^{20} 1·435).

4-*Vinyl*cyclo*hexene* (Expts. 73—74).—Addition of slightly more than 1 molar proportion of hydrogen peroxide by method B gave, in good yield, 4-*vinyl*cyclo*hexane*-1 : 2-*diol*, b. p. 112—115°/1 mm., m. p. 29—33·5°, n_D^{20} 1·5027 (Found : C, 67·4; H, 9·9. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%). The *bis*-3 : 5-*dinitrobenzoate*, crystallised from benzene–light petroleum, had m. p. 83—85° (Found : C, 49·0; H, 3·4. $C_{22}H_{18}O_{12}N_4$ requires C, 48·5; H, 3·4%). Addition of rather more than 2 moles of hydrogen peroxide to the diene afforded a product, which was isolated by salting out with potassium carbonate and extraction with *n*-butanol. After reprecipitation several times from cold ethanolic solution by addition of acetone it formed a hygroscopic amorphous mass, presumed to be the tetraol (4-1′ : 2′-hydroxyethyl*cyclo*hexane-1 : 2-diol). This could also be obtained in small yield by the sluggish reaction of the diol with hydrogen peroxide and pertungstic acid in aqueous solution at 70° (Expt. 52). A further account of these compounds, including proofs of structure, will be given later (Abbott and Faulkner, to be published).

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