nones and maleic anhydride in the Diels–Alder reaction. It is not likely that the monomer units in copolymerization actually add to the growing chain as charged particles. However, any tendency of two monomers to act as electron donor and electron acceptor, respectively,[28] would be reflected in the contributions of corresponding resonance structures and resultant polarities, both in the monomers themselves and in the radicals terminating in them. Probably the explanation of the selectivity in copolymerization of allyl acetate and maleic anhydride is to be sought along these lines. The scarcity of monomers which behave like maleic anhydride would then be due to the fact that most substances with a similar ability to accept electrons (including the quinones) have enough additional resonance possibilities to make them chain inhibitors rather than copolymerizers. To be highly selective in the manner of maleic anhydride and yet not an inhibitor requires rather narrow limits of resonance stabilization in molecule and radical.

Summary

Maleic anhydride is polymerized at 55° by benzoyl peroxide, about 29 monomer molecules being polymerized for each peroxide molecule decomposed.

Allyl acetate and maleic anhydride undergo rapid and highly selective copolymerization in the presence of benzoyl peroxide. The copolymerization is more rapid at 30° than the polymerization of either of the monomers separately at 80°. The peroxide decomposition under these conditions is largely induced by chain transfer, being 196 times as rapid as in allyl acetate alone. For each peroxide molecule decomposed, 187–427 molecules of monomer are polymerized, compared with not over 36 for allyl acetate separately under the same conditions, and a similar figure for maleic anhydride.

The copolymer is insoluble in the mixture of monomers and shows only limited solubility in all solvents except water. The copolymer prepared with 4.58% by weight of benzoyl peroxide, a great excess of peroxide, has a molecular weight of about 40,000 in acetone; copolymers prepared with lower peroxide concentrations are too insoluble for osmotic pressure measurements. Measurements in water are difficult to interpret because of ionization of the carboxyl groups in the hydrolyzed polymer.

A study of copolymers prepared with *p*-chlorobenzoyl peroxide has been made and it is concluded that only about one out of four peroxide molecules decomposing leads to the attachment of a fragment to the polymer.

A survey of a few other copolymerizations shows none with the degree of tendency toward 1:1 copolymerization exhibited by this system, which yields a 1:1 copolymer even when the ratio of monomers is originally 1:5 and 5:1. This selectivity is not correlated with any abnormal vapor pressures, solubilities, or viscosities of the monomer mixtures.

The results are interpreted in terms of the mechanism of polymerization, as far as the experimental limitations permit.

CAMBRIDGE 38, MASSACHUSETTS

RECEIVED[29] APRIL 24, 1946

---

[28] Compare Gibson and Loeffler, THIS JOURNAL, **62**, 1324 (1940).

[29] Original manuscript received September 12, 1945.

[CONTRIBUTION FROM EASTERN REGIONAL RESEARCH LABORATORY[1]]

Hydroxylation and Epoxidation of Some 1-Olefins with Per-acids

BY DANIEL SWERN, GERALDINE N. BILLEN AND JOHN T. SCANLAN

In previous publications from this Laboratory, the quantitative hydroxylation of mono-unsaturated fatty materials with hydrogen peroxide in formic acid solution[2] and epoxidation with peracetic acid in acetic acid solution,[3] respectively, were reported. The purpose of the present publication is to describe the results obtained when these reactions were applied to straight-chain, 1-olefins.

In our earlier paper,[2] it was tentatively concluded that the hydrogen peroxide–formic acid hydroxylation reaction, in which formic acid serves the dual purpose of solvent and oxygen carrier (performic acid is the intermediate compound), is a general method for the hydroxylation of mono-unsaturated compounds with isolated ethylenic linkages. In seeking further confirmation of this conclusion, we have applied this reaction to 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene and 1-octadecene, and we have found that good yields of 1,2-glycols are obtained when only 1.025 to 1.05 moles of hydrogen peroxide is employed for each mole of olefin. The crude, saponified reaction products, obtained in yields of 70% or more, usually consisted of almost pure 1,2-glycols without further treatment. The pure glycols, obtained in yields ranging from 40 to 70%, were isolated either by fractional distillation or by recrystallization from

---

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] Swern, Billen, Findley and Scanlan, THIS JOURNAL, **67**, 1786 (1945).

[3] Findley, Swern and Scanlan, *ibid.*, **67**, 412 (1945).

TABLE I

1,2-GLYCOLS OBTAINED BY HYDROXYLATION OF THE C_8 TO C_{18} STRAIGHT-CHAIN 1-OLEFINS WITH HYDROGEN PEROXIDE AND FORMIC ACID

	Crude glycols			Purified glycols							
						Carbon, %		Hydrogen, %		Hydroxyl, %[b]	
1,2-Glycol	Yield, %	Iodine no.	M. p.,[a] °C.	Yield, %	M. p., °C.	Calcd.	Found	Calcd.	Found	Calcd.	Found
Octanediol	70	1	<25	58	30–30.5[c]	65.7	65.3	12.4	12.4	23.2	23.0
Decanediol	75	1	45–48	45	48–49	68.9	69.2	12.7	12.8	19.5	19.3
Dodecanediol	75	1	58–59	40	60–61	71.3	72.1	13.0	12.8	16.8	16.5
Tetradecanediol	95	4	65	69	68–68.5	73.0	73.4	13.1	13.1	14.8	14.5
Hexadecanediol	100	14	68–69	58	75–76[d]	..	..	..	..	..	..
Octadecanediol	100	21	73.5–74	50	80–81[d]	..	..	..	..	..	..

[a] Melting points were determined in a capillary tube attached to a calibrated thermometer immersed in an air-bath whose temperature was raised 0.5° per minute. Usually somewhat higher melting points were obtained when the rate of heating was doubled. [b] Determined by the method of Ogg, Porter and Willits, *Ind. Eng. Chem., Anal. Ed.*, **17**, 394 (1945). [c] Boiling point, 135–136° (10 mm.). [d] Previously reported by Niemann and Wagner.[5]

methanol to constant melting point. They are white, odorless, crystalline solids soluble in all the common organic solvents. The shorter chain glycols are slightly soluble and dispersible in water, but those containing more than fourteen carbon atoms are not. The results of our investigation are summarized in Table I. It should be noted that the yield of crude glycols increases as the chain is lengthened. We believe that this is due to lower processing losses, attributable to decrease in water solubility.

Although the older literature contains reference to octanediol and decanediol,[4] it is doubtful whether the products reported consisted exclusively of the straight-chain 1,2-glycols, since the purity of the olefins employed as the starting materials is questionable and the properties do not entirely agree with those of the 1,2-glycols which we have prepared from purified 1-octene and 1-decene. 1,2-Hexadecanediol and 1,2-octadecanediol have been prepared by other workers from 1-hexadecene and 1-octadecene by a synthetic method which differs from ours.[5] No reference could be found in the literature to 1,2-dodecanediol and 1,2-tetradecanediol.

A major difference between the hydroxylation of the mono-unsaturated fatty materials reported previously[2] and the unsaturated hydrocarbons is the length of time required for completion of the reaction, the former compounds requiring two to four hours, the latter eight to twenty-four. That the slowness of hydroxylation of the hydrocarbons is not due to the position of the double bond at the end of a long chain is shown by the fact that hendecenoic (undecylenic) acid, which also has a terminal double bond, reacts completely with hydrogen peroxide in formic acid solution in two to four hours. The longer reaction time appears to be related to the low solubility of the hydrocarbons and their oxidation products in formic acid. Thus, the hendecenoic acid hydroxylation mixture became homogeneous in about one hour, and the reaction was complete about two hours later. In the case of 1-octene, the reaction was also complete two hours after the mixture became homogeneous, but it required six hours to become homogeneous. The much less soluble longer-chain hydrocarbons required twenty-four hours reaction time, and at no time were the reaction mixtures homogeneous, even though in some instances double the usual quantity of formic acid was used.

The epoxidation of the hydrocarbons with peracetic acid in acetic acid solution gave only moderately satisfactory results. Whereas similar epoxidation of long-chain, mono-unsaturated fatty materials[3] usually gave fairly complete conversion to oxirane derivatives in a few hours, the hydrocarbons reacted very slowly (twenty-four to thirty hours at room temperature) and only about 40 to 60% conversion to 1,2-epoxides was obtained. The hydrocarbon epoxidation reaction products consisted of about 40 to 60% epoxide, 5 to 25% unreacted hydrocarbon and 15 to 40% hydroxy-acetoxy compounds. Since the oxirane ring is opened by glacial acetic acid at the rate of 1% per hour at 25°,[3] the formation of a large proportion of hydroxy-acetoxy compounds was not surprising. By vacuum fractional distillation of the crude C_8 to C_{14} epoxidation products, it was easily possible to obtain 35 to 55% yields of pure 1,2-epoxides. The lower boiling fractions consisted mainly of unreacted hydrocarbon, which could be re-used. The distillation residues consisted mainly of the hydroxy-acetoxy compounds, which have considerably higher boiling points than either the olefins or the epoxides. We were not able to obtain pure 1,2-epoxyhexadecane or 1,2-epoxyoctadecane either by this technique or by fractional crystallization of the crude epoxidation products. Vacuum distillation yielded products of only 80 to 90% purity, as determined by oxirane–oxygen analysis.[6] The epoxides are insoluble in water and soluble in all the common organic solvents. The C_8 to C_{16} epoxides are colorless liquids, which vary considerably in odor. The C_8 and C_{10} compounds have fruity odors, the C_{12} and C_{14} smell like gasoline, and the C_{16} is odorless. The C_{18} epoxide is an odorless, hard, white, crystalline solid. The results are summarized in Table II.

---

(4) Prileschajew, *Ber.*, **42**, 4811 (1909).

(5) Niemann and Wagner, *J. Org. Chem.*, **7**, 227 (1942).

(6) Nicolet and Poulter, THIS JOURNAL, **52**, 1186 (1930).

TABLE II

1,2-EPOXIDES OBTAINED BY EPOXIDATION OF THE C_8 TO C_{18} STRAIGHT-CHAIN 1-OLEFINS WITH PERACETIC ACID

	Composition of crude epoxidation products,			Purified epoxides						
1,2-Epoxide	Epoxide	% Hydroxyacetate	Unreacted olefin	Yield, %	B. p., °C.	B. p., Mm.	Oxirane-oxygen, % Calcd.	Oxirane-oxygen, % Found	$n^{20}D$	d^{20}_4
Epoxyoctane	50	40	6	35	61 119	15 45	12.5	12.0	1.4193	0.839
Epoxydecane	60	23	15	56	89	10	10.2	10.0	1.4288[a]	.842[a]
Epoxydodecane	60	21	18	52	97–98	3.5	8.68	8.53	1.4356[a]	.844[a]
Epoxytetradecane	60	21	14	42	95–96	0.4	7.54	7.53	1.4405	.845
Epoxyhexadecane	56	14	25	50	104–106	0.2	6.66	5.98	....	...
Epoxyoctadecane	41	15	40	44	137	0.5	5.96	4.81	....	...

[a] Previously reported by Rothstein.[7]

1,2-Epoxydecane, 1,2-epoxydodecane and 1,2-epoxyhexadecane have been previously prepared by synthetic methods which differ from ours.[7,8] Although epoxyoctane has been reported previously,[4] it is doubtful, for the reasons mentioned earlier in this paper, that the straight-chain 1,2-epoxide was obtained. No literature reference to 1,2-epoxytetradecane and 1,2-epoxyoctadecane could be found.

The slow rate of epoxidation of these hydrocarbons is rather surprising, since one would expect compounds with a double bond at the end of a carbon chain to react more rapidly than those with a double bond in the middle of a long chain. This cannot be attributed to solubility, since 1-hexadecene and 1-octadecene, which are only slightly soluble in the acetic acid solution, reacted at the same rate as 1-octene and methyl hendecenoate,[3] both of which are extremely soluble in the oxidizing solution.

Experimental

Starting Materials.—The terminally unsaturated hydrocarbons 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene and 1-octadecene, supplied by the Connecticut Hard Rubber Company, were fractionally distilled through a column 50 cm. long and 2 cm. in diameter, packed with $^3/_{32}$-inch single-turn glass helices. The products employed in the reactions described below agreed in boiling point and refractive index with the best values in the literature.[9,10] Peracetic acid solution was prepared as previously described.[3]

Hydroxylation with Hydrogen Peroxide–Formic Acid.—Since the hydroxylation procedure is substantially the same for all the hydrocarbons, details will be given for the preparation of 1,2-tetradecanediol only. To a well-stirred mixture of 49.2 g. (0.25 mole) of 1-tetradecene and 295 ml. of formic acid (98 to 100% grade) at room temperature, 35 g. of 25.6% hydrogen peroxide (0.263 mole; 5% excess) was added in one portion. The mixture was heated and stirred at 40° for about twenty-four hours, at which time an analysis[11] revealed that slightly more than the theoretical quantity of peroxide had disappeared. The reaction mixture was heterogeneous throughout. The formic acid was recovered under reduced pressure, and the distillation residue was refluxed for about one hour with excess 3 *N* alcoholic potassium hydroxide. Most of the alcohol was evaporated, and a large excess of hot water was added to precipitate the crude glycol. When the mixture had cooled to room temperature, the aqueous layer was siphoned off. The hot-water wash was repeated until the crude glycol was alkali free. The washings were extracted with ether to remove a small quantity of dissolved glycol, and the residue obtained after evaporation of the ether was combined with the water-washed product. The yield of crude (fairly pure) 1,2-tetradecanediol was about 55 g. (95%); iodine number, about 4; m. p. 65°. Recrystallization from methanol (8 ml./g.) to constant melting point yielded about 40 g. (69%) of pure 1,2-tetradecanediol; m. p. 68–68.5°.

For the hydroxylation of the other hydrocarbons the procedure was the same, with the following exceptions.

The 1-octene, 1-decene and 1-dodecene reaction mixtures contained a 2.5% molar excess of hydrogen peroxide and only 3 ml. of formic acid per gram of olefin. The 1-octene hydroxylation mixture became homogeneous after about six hours at 40°, and the reaction was complete about two hours later. Crude 1,2-octanediol, which is liquid at room temperature, was purified by vacuum distillation through an 18-inch Vigreux column. Its boiling point is 135–136° (10 mm.). The results of the hydroxylations are summarized in Table I.

Epoxidation with Peracetic Acid in Acetic Acid Solution.—Since the epoxidation procedure is substantially the same for all the hydrocarbons, details will be given for the preparation of 1,2-epoxydodecane only. A mixture of 50.5 g. (0.3 mole) of 1-dodecene and 408 g. of approximately 0.9 *M* peracetic acid solution (0.36 mole) was stirred at 20–25° for twenty-eight hours, at which time about 80 to 85% of the theoretical quantity of peracetic acid had disappeared. The reaction solution became homogeneous after about eight hours. The reaction mixture was poured into cold water, and the product was extracted with ether. The ether extract was washed several times with water, and the ether was evaporated. The residue (composition shown in Table II) was distilled through an 18-inch Vigreux column and yielded about 29 g. (52%) of 1,2-epoxydodecane, b. p. 97–98° (3.5 mm.), $n^{20}D$ 1.4356; oxirane-oxygen calcd., 8.68; found, 8.53.

For the epoxidation of the other hydrocarbons the procedure was the same, with the following exceptions.

The 1-octene and 1-decene reaction mixtures were homogeneous from the start, whereas the 1-tetradecene, 1-hexadecene and 1-octadecene reaction mixtures required the addition of further quantities of acetic acid before becoming homogeneous. The fractional distillation of 1,2-epoxydecane was carried out through a column which was 73 cm. long and 0.6 cm. in diameter and contained a spiral stainless steel, screen packing. 1,2-Epoxyhexadecane and 1,2-epoxyoctadecane could not be purified either by crystallization of the crude expoxidation products or by fractional distillation. Distillation through an 18-inch Vigreux column yielded products of only 80 to 90% purity. The results are summarized in Table II.

---

(7) Rothstein, *Bull. soc. chim.*, [5] **2**, 1936 (1935).

(8) von Braun, *Ber.*, **56**, 2178 (1923).

(9) Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., N. Y., 1939.

(10) Doss, "Physical Constants of the Principal Hydrocarbons," 4th ed., The Texas Co., N. Y., 1943.

(11) Wheeler, *Oil & Soap*, **9**, 89 (1932).

Summary[12]

Six straight-chain 1-olefins, namely, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene and 1-octadecene, were hydroxylated with hydrogen peroxide in formic acid solution (performic acid is the oxidizing agent) and gave good yields of the corresponding 1,2-glycols. Only 1.025 to 1.05 moles of hydrogen peroxide was required for each mole of olefin. 1,2-Octanediol, 1,2-decanediol, 1,2-dodecanediol and 1,2-tetradecanediol were prepared for the first time.

The same olefins were epoxidized with peracetic acid in acetic acid solution but gave only fair yields of the corresponding 1,2-epoxides. 1,2-Epoxyoctane, 1,2-epoxytetradecane and 1,2-epoxyoctadecane were prepared for the first time.

PHILADELPHIA 18, PA. RECEIVED APRIL 12, 1946

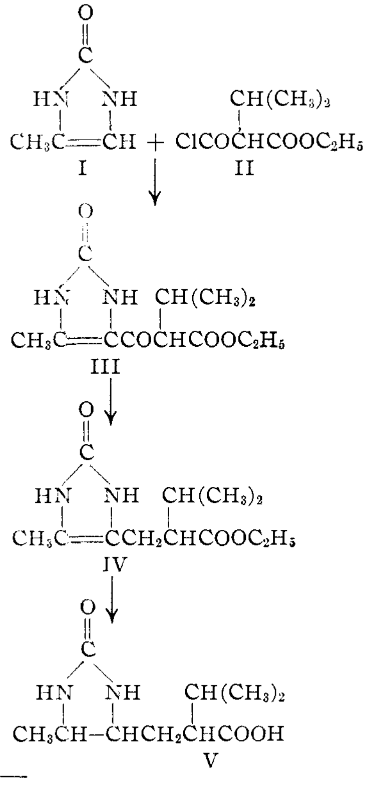
[12] Presented at the 109th meeting of the American Chemical Society, Division of Organic Chemistry, April 8–12, 1946, at Atlantic City, New Jersey.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, CORNELL UNIVERSITY MEDICAL COLLEGE]

α-Isopropyl-5-methyl-2-oxo-4-imidazolidinepropionic Acid, A Structural Isomer of Desthiobiotin[1,2]

BY GEORGE BOSWORTH BROWN AND MARTHA F. FERGER

The synthesis of a structural isomer of desthiobiotin, namely, α-isopropyl-5-methyl-2-oxo-4-imidazolidinepropionic acid (V), has been accomplished. This isomer of desthiobiotin corresponds to that which would be derivable from the revised structure of the "egg-yolk biotin," or "α-biotin" as proposed by Kögl and Borg.[3] The condensation of 4-methylimidazolone-2 (I) and ethyl α-chloroformylisovalerate (II), was carried out by the method of Duschinsky and Dolan,[4] followed by the stepwise reduction of the resulting ketone (III).



The final reduction of IV was carried out over both platinum and over Raney nickel catalysts. The reduction of a similar imidazolone over platinum led[4] to a preferential *cis* reduction and the production of *dl*-desthiobiotin, while over Raney nickel[5] the same imidazolone yielded both the *dl* and *allo* isomers of desthiobiotin. With the additional asymmetric center in the present molecule these two methods of reduction could be expected to lead, respectively, to two and four racemic isomers. One crystalline form of V has been obtained in reasonable yield from the reduction over platinum and the same form has been obtained in small yield from the reduction over Raney nickel.

The crystalline form of V as well as the unfractionated products from the reductions over each catalyst were assayed in biotin-deficient media with *Saccharomyces cerevisiae*[6] and *Lactobacillus casei*.[7] No growth-promoting activity was found. They were also tested for antibiotin activity for *L. casei* and no inhibition of growth was observed.

Experimental[8]

Ethyl α-Chloroformylisovalerate (II).—A solution of 320 g. of ethyl malonate in 1 liter of absolute ethanol containing 46 g. of sodium was alkylated with 246 g. of isopropyl bromide. The conversion of this ester to the mono acid and mono acid chloride was accomplished by the method used by Staudinger and Bereza[9] for the ethyl analog.

---

[1] The authors wish to express their appreciation to Lederle Laboratories, Inc., for a research grant which has aided greatly in this work.

[2] The authors also wish to thank Mrs. Mary McKee for assistance with the yeast assays and Dr. J. R. Rachele for the microanalyses reported here.

[3] Kögl and Borg, *Z. physiol. Chem.*, **281**, 65 (1944).

[4] Duschinsky and Dolan, THIS JOURNAL, **67**, 2079 (1945).

[5] Wood and du Vigneaud, *ibid.*, **67**, 210 (1945).

[6] Biotin and desthiobiotin have equal growth-promoting activities for yeast; Melville, Dittmer, Brown and du Vigneaud, *Science*, **98**, 497 (1943).

[7] Desthiobiotin inhibits the growth of *L. casei* and this inhibition may be reversed by sufficient biotin; (a) Dittmer, Melville and du Vigneaud, *ibid.*, **99**, 203 (1944); (b) Lilly and Leonian, *ibid.*, **99**, 205 (1944).

[8] Melting points were determined on a micro melting point block.

[9] Staudinger and Bereza, *Ber.*, **42**, 4908 (1909).