327. *Catalytic Properties of the Phthalocyanines. Part III.*

By A. H. Cook.

The oxidation of a number of olefinic compounds by oxygen in presence of iron phthalocyanine, yielding products containing a carbonyl group and only rarely a hydroxyl group adjacent to the double linkage, has been studied. Structural factors and the formation of an intermediate peroxide of the compound being oxidised are indicated. The catalyst functions partly by promoting the formation of the peroxide and partly by accelerating its further rearrangement to a ketone.

THE ability of iron phthalocyanine and similar pigments to decompose hydrogen peroxide catalytically was discussed in Part I, and the effect found to be quantitatively comparable with that of hæmin, *i.e.*, intermediate between those of the enzyme catalase and of ionised iron salts. The behaviour of organic peroxides towards iron compounds, however, presents further possibilities of elucidating the rôle of the catalyst and the mechanism of the ensuing reaction. Catalase itself, the activity of which is due to an iron porphyrin associated with a protein carrier, is, unlike ionised iron, unable to catalyse the decomposition of dialkyl peroxides (Stern, *Z. physiol. Chem.*, 1932, **209**, 176), and a study of the behaviour of iron pigments of the phthalocyanine and porphyrin classes will form the subject of a future paper. In the present paper, the action of the phthalocyanines towards some miscellaneous peroxides, and in reactions in which the formation of peroxides almost certainly plays an important part, has been investigated.

Tetralin was of particular interest in that it is one of the few easily accessible compounds known to form unimolecular peroxides. Its peroxide (I; see p. 1777) was prepared by the method of Hock and Susemihl (*Ber.*, 1933, **66**, 61) (see also Hartmann and Seiberth, *Helv. Chim. Acta*, 1932, **15**, 1390). In the supercooled or the dissolved state it proved to be extraordinarily sensitive towards iron phthalocyanine, a mere trace of which caused considerable evolution of heat. This property is possessed to a somewhat similar degree by iron octaphenylporphyrazin and to a less extent by hæmin. The effect is illustrated by the following experiments under arbitrary conditions, the temperature of 1 g. of tetralin peroxide in 1 c.c. of benzene being determined at intervals (in minutes) after addition of the catalysts named. (The experiments were purely qualitative and no attempt was made to measure accurately the heat generated.)

$FeCl_3$, 100 mg.		Iron phthalocyanine, 20 mg.		Iron phthalocyanine, 5 mg.		Iron octaphenylporphyrazin, 20 mg.		Hæmin, 50 mg.	
Time.	Temp.	Time.	Temp.	Time.	Temp.	Time.	Temp.	Time.	Temp.
0	20·5°	0	20·5°	0	20·5°	0	20·5°	0	20·5°
2	26	0·5	30	1	27	3	28	Very slight evolution of heat	
4	32	0·75	60	2	40·5	5	25		
6	36·5	1·0	Boiling	3	50				
8	38·5								

Of 38 other metal phthalocyanines and related pigments examined, all were quite inactive except chromium and cobalt phthalocyanines, which were very feebly active. The effect is the more remarkable when it is remembered that tetralin peroxide alone exhibits no tendency to decompose even at 100° (Yamada, *Chem. Zentr.*, 1937, II, 3158).

This behaviour of iron pigments recalls the conversion of tetralin peroxide into α-tetralone by the somewhat feeble action of ferrous sulphate (Hartmann and Seiberth, *loc. cit.*), by sodium hydroxide (Hock and Susemihl, *loc. cit.*), and particularly by iron pentacarbonyl (Mittasch, *Z. angew. Chem.*, 1928, **41**, 829). In the present instance the products were approximately 1 part of α-tetralone and 2 parts of high-boiling material, presumably arising by intermolecular condensation of the first-formed ketone. The action of the iron pigments is, of course, exerted on any tetralin preparation containing peroxide such as is obtained by autoxidation of tetralin.

As current methods of oxidising tetralin to α-tetralone (chromic acid) and of effecting similar conversions are in many respects unsatisfactory, these observations were developed to provide an improved means of preparing such ketones; *e.g.*, 465 g. of tetralin were oxidised in presence of 100 mg. of iron phthalocyanine, 48% being recovered unchanged and 31% converted into α-tetralone.

In this and in the reactions described below, catalysis is accompanied by the rapid disappearance of the blue-green iron pigment. When other metallic pigments are added which fail to induce reaction they remain suspended in the peroxide solution quite unattacked. The products of iron-pigment reactions are thus always orange-brown, owing possibly in part to colloidal oxide of iron. It is remarkable, however, that such a solution containing degraded or modified phthalocyanine is still as active towards tetralin peroxide as the original pigment, and it seems that a given quantity of pigment is able to decompose an almost unlimited quantity of peroxide with an efficiency unapproached by other iron compounds; relatively large amounts of anhydrous ferric chloride were only slightly active, although soluble in the organic medium.

There is, in addition, strong evidence that the primary active catalyst is not merely an active form of iron oxide, but a peroxide addition product of iron phthalocyanine or perhaps an oxygenated iron phthalocyanine, although this does not exclude the possibility of simple degradation products contributing in small measure to the total catalytic effect. For instance, when a peroxide solution (*e.g.*, tetralin peroxide in benzene) is shaken with iron phthalocyanine, appreciable quantities of pigment pass into solution to yield a clear red-brown liquid in which no phthalocyanine can be detected spectroscopically. The green colour and phthalocyanine spectrum quickly reappear, however, on shaking with a reducing agent (hydrazine) and pyridine, the latter behaving as a solvent only. It may be concluded, therefore, that the essential feature of these catalyses is the formation of a transient compound of the peroxide with the catalyst, which may itself function in an oxygenated form so that the internal oxidation–reduction, as the present reactions may be formulated, requires a lower activation energy.

Again, old specimens of Δ^2-octalin evolved heat when brought into contact with iron phthalocyanine, a phenomenon undoubtedly due to their peroxide content. Although a unimolecular peroxide was not prepared, Δ^2-octalin was oxidised by a process similar to that employed in the preparation of α-tetralone, allowing the continuous formation and catalytic decomposition of peroxide. Again, the main oxidation product was a ketone—the hitherto unknown Δ^2-*α-octalone*. The yield, without allowance for the 30% of recovered hydrocarbon, was again approximately 30%. Reduction yielded α-decalone.

The formation of a " moloxide " by pinene has been extensively investigated, and its catalytic oxidation to verbenol and polymeric material in presence of metallic oxides, etc., has also been studied (Wienhaus and Schumm, *Annalen*, 1924, **439**, 31; Dupont and Crouzet, *Bull. Inst. Pin.*, 1929, Spec. No. 101; Suzuki, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1935, **14**, 14; 1936, **15**, 70). It is now found that oxidation of α-pinene in presence of iron phthalocyanine with air or oxygen at a slightly elevated temperature yields a mixture of verbenone, verbenol, and polymeric material. The total yield of material of low molecular weight was again only 30%, of which the greater part was not ketonic.

Oxidation of *cyclo*hexene proceeds similarly, with formation of a peroxide which, in presence of iron phthalocyanine, undergoes secondary change. The absorption of oxygen in presence of several catalysts (*e.g.*, ferric oxide) has been observed (Berl, Heise, and Winnacker, *Z. physikal. Chem.*, 1928, *A*, **139**, 453), and in particular the use of osmium oxide has led to fairly well-defined products of low molecular weight (Δ^2-*cyclo*hexenol, *cyclo*pentenealdehyde) (Willstätter and Sonnenfeld, *Ber.*, 1913, **46**, 2953; Kötz and Richter, *J. pr. Chem.*, 1925, **111**, 373; Medvedev and Alexejeva, *Chem. Zentr.*, 1927, II, 1012). In the present work it was found that substantially the same result is obtained when the osmium oxide is replaced by iron phthalocyanine. The absence of ketonic products in this case is remarkable, particularly as Δ^1-methyl*cyclo*hexene when similarly treated yielded approximately 40% of a mixture of Δ^1-methyl*cyclo*hexen-3-one and the corresponding alcohol.

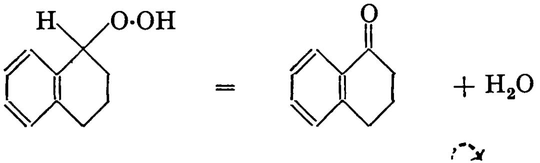
Other compounds containing a reactive methylene group proved to be oxidisable by oxygen in presence of iron phthalocyanine; *e.g.*, diphenylmethane was oxidised cleanly to benzophenone. Cholesterol was expected to undergo oxidation in the same manner as simpler cyclic olefins to yield compounds containing additional carbonyl or hydroxyl groups, but experiments with this compound were without useful result, its solution in benzene dissolving abnormal quantities of iron phthalocyanine but absorbing practically no oxygen in presence of the catalyst even after several hours at 80°. The dihydrogen phosphoryl ester also failed to react in the expected manner, but after acetylation of the free hydroxyl group oxidation became rapid. The chief product, apart from the complex mixture presumably formed by the interaction of first-formed oxidation products, was 7-ketocholesteryl acetate. Simple aliphatic olefins (*e.g.*, Δ^2-*n*-pentene, trimethylethylene) could not be oxidised by the procedure described.

The mechanism of these oxidations is of considerable interest in its bearing on the function of iron and other heavy metals in natural processes and catalytic oxidations generally.

According to current conceptions, the direct oxidation of an organic compound in solution by gaseous oxygen may proceed by way of one or more of several paths: (1) The oxygen may function simply as an acceptor of hydrogen, which is therefore oxidised to hydrogen peroxide; the dehydrogenation may, according to the lability of the hydrogen involved, proceed spontaneously or require the added activation of iron or other heavy-metal catalyst which may simultaneously decompose hydrogen peroxide as it is formed. (2) The presence of an iron or other catalyst in which the valency of the metal is variable will further the oxidation when a cycle in which the oxidised form of the catalyst is continually reduced by the substrate itself is set up. (3) Oxygen may be supplied to the organic substrate through an intermediate metal peroxide. (4) Direct addition of oxygen to the organic compound, possibly with the aid of metallic catalysts, may lead to the formation of organic peroxides, which may themselves take a leading part in the oxidation (cf. the oxidation of benzaldehyde *via* perbenzoic acid, p. 1778). (5) Reaction chains may be initiated by the reduction of a tervalent iron catalyst by the substrate, the catalyst being then reoxidised by oxygen.

In the case of the phthalocyanines, mechanisms (2) and (5) can only be speculative, in that evidence of the interconversion of ferrous and ferric pigments is obscure (cf. this vol., p. 1156); ferrous phthalocyanine emerges unchanged from the most drastic treatment, and it is therefore difficult to imagine that it takes part in any such cyclic change under the mild conditions obtaining in the present experiments. Of the remaining possibilities, (3) and (4) may be considered. In the case of tetralin peroxide, however, the unimolecular peroxide is known to be formed in absence of additional iron phthalocyanine, if not in absence of all trace of heavy metal, so the effect of the added metal complex is not, at least to a major extent, to promote the primary reaction with oxygen, but rather to bring about an internal oxidation–reduction of the peroxide :

(I.)



(cf. the catalytic decomposition of hydrogen peroxide : $2H\overset{\curvearrowright}{OO}H = 2H_2O + O_2$).

In other cases there is similar direct evidence that the reaction of the peroxide is facilitated in presence of iron phthalocyanine, and it may legitimately be assumed that the oxidation of other reactive olefins proceeds through the formation of peroxides, and that the function of the catalyst is to fix the oxygen by promoting further interaction.

The primary products (*i.e.*, those of low molecular weight) of these catalytic oxidations may in every case be anticipated by the insertion of a hydroxyl or carbonyl group on a carbon atom adjacent to the double bond. Activation of the methylene group by proximity to a double bond is certainly one, but not necessarily the sole, structural factor conditioning the susceptibility of a organic compound towards catalytic oxidations of this type. Thus, although in the present examples, cyclic olefins and even hydrocarbons such as tetralin and diphenylmethane, where the double bond may in a narrow sense be regarded as part of an aromatic system, were readily oxidised, yet purely aliphatic olefins were resistant to the attack of oxygen in presence of iron phthalocyanine. In cholesterol the effect of the double linkage was more than counteracted by the comparatively remote hydroxyl group at C_3, an influence which is sufficiently weakened to permit oxidation on esterification with acetic acid but not with phosphoric acid.

Finally, it is noteworthy that the results of the present oxidations by means of iron phthalocyanine and oxygen are almost exactly paralleled as far as the dual experiments have been carried out (cf. Treibs and Schmidt, *Ber.*, 1928, **61**, 459) by those using chromic acid, a finding which recalls the view that the latter oxidations proceed through an intermediate peroxide–metal complex.

On consideration of catalysed oxidations of aldehydes (benzaldehyde) such as are described in Part II, three broad views are apparent :

(1) The catalytic oxidation of aldehydes to acids proceeds, according to Haber and Willstätter (*Ber.*, 1931, **64**, 2844; see also Haber and Weiss, *Naturwiss.*, 1932, **20**, 948; *Proc. Roy. Soc.*, 1934, *A*, **147**, 332; cf. Weiss, *J. Physical Chem.*, 1937, **41**, 1107) by a radical chain process :

$$R{\cdot}CHO + OH' \longrightarrow H_2O + R{\cdot}CO'$$

$$R{\cdot}CO' + O_2 \longrightarrow RC\Big\langle{}^{O}_{O\cdot O'}$$

$$R{\cdot}C\Big\langle{}^{O}_{O\cdot O'} + R{\cdot}CO' + H_2O \longrightarrow 2R{\cdot}CO_2H + OH'$$

(2) Wieland *et al.* (*Annalen*, 1927, **457**, 1; 1928, **464**, 101; **475**, 1; 1934, **509**, 1; see also Wieland, " On the Mechanism of Oxidation," 1934) adduce evidence to show that, in some instances at least, catalytic oxidation by metals is essentially, as a result of complex form-

ation, a result of activation of hydrogen, which can then be transferred to oxygen or other hydrogen acceptors (*e.g.*, methylene-blue). In the present instance no reduction of methylene-blue by the phthalocyanine–benzaldehyde system could be observed under widely different conditions but always in absence of oxygen. The latter stages of catalysis may, if extensive degradation of the pigment actually takes place, be ferrous–ferric catalyses of the ordinary induced type (Wieland and Franke, *Annalen*, 1928, **464**, 101), although the magnitude of the effect would probably not be comparable with the direct effects noted.

(3) Manchot (*Z. anorg. Chem.*, 1933, **211**, 1) postulates intermediate peroxidic iron compounds which can revert to the tervalent and under some conditions to the bivalent state—a postulate which receives experimental support from the work of Krause (*Ber.*, 1935, **68**, 1734).

The autoxidation of benzaldehyde in particular has also been formulated as a two-stage process:

$$\mathrm{Ph{\cdot}CHO} + \mathrm{O_2} \longrightarrow \mathrm{Ph{\cdot}CO_3H}$$
$$\mathrm{Ph{\cdot}CO_3H} + \mathrm{Ph{\cdot}CHO} \longrightarrow \mathrm{2Ph{\cdot}CO_2H}$$

This mechanism has been criticised (Meyer, *J. Biol. Chem.*, 1933, **103**, 35) on the ground that the supposed intermediate perbenzoic acid decomposes as readily in presence as in absence of benzaldehyde, and always with evolution of oxygen. Perbenzoic would, however, be formed in intimate association with both catalyst and benzaldehyde, and inability experimentally to reconstruct this association from pre-formed perbenzoic acid is not sufficient to warrant rejection of the general mechanism. Such association very probably occurs in the case of phthalocyanine catalysis, for when benzaldehyde, water, and iron phthalocyanine are shaken in air, the suspension on dilution with pyridine shows an absorption spectrum with bands similarly placed to, but of different relative intensities from, those observed with the pigment alone; the spectrum reverts to normal on slight warming, and the abnormality cannot be made to reappear on reoxygenation of the pyridine solution; it is perhaps significant that van der Bech (*Rec. Trav. chim.*, 1928, **47**, 286) could detect no peroxide formation on oxidising benzaldehyde in pyridine solution.

The autoxidation of benzaldehyde in presence of phthalocyanine thus comprises at least two concurrent catalyses: (*a*) a simple transference of oxygen, possibly direct and in the Manchot sense, and simultaneously (*b*) an autocatalysed oxygenation of the phthalocyanine pigment itself, with formation either of a highly active intermediate or of a particularly active colloidal oxide of iron, this secondary oxidation being very considerably retarded when the pigment is in association with barium sulphate.

It seems that the stability of hæmin and other iron porphyrins when employed as oxidative catalysts is of a somewhat higher order than that of the iron phthalocyanines, but a tendency towards decomposition is still quite marked (cf. Kuhn and Brann, *Ber.*, 1926, **59**, 2370). The oxidation of iron complexes is unique among pigments of the metal phthalocyanine group in that it is only observed when the iron pigments are actively engaged in transferring oxygen. Alone, in air, in aqueous suspension, or under drastic acid or alkaline conditions, they exhibit the same remarkable stability as other phthalocyanines.

EXPERIMENTAL.

Oxidation of Tetralin.—465 G. of tetralin were warmed to 70° with 100 mg. of iron phthalocyanine (the amorphous product obtained by precipitating a solution in concentrated sulphuric acid is most suitable), a very slow stream of air or oxygen being passed through the liquid. A long air-condenser minimised loss of tetralin. After 12 hrs., all phthalocyanine had disappeared, and after 3 days a quantity of water had separated from the orange-brown product. Oxidation was discontinued after 6 days, immediate distillation yielding 225 g. of tetralin and 165 g. of α-tetralone, b. p. 120°/4 mm. The semicarbazone, m. p. 214—217° after two crystallisations from alcohol, did not depress the m. p. of an authentic specimen.

It appeared possible that the polymeric material arises by intermolecular condensation of primarily formed ketone, but although this last reaction is known to proceed less readily in acid media, the products of oxidation were not substantially different when acidity was ensured by adding a small quantity of acetic acid.

Oxidation of Δ^2*-Octalin.*—10 G. of Δ^2-octalin containing 50 mg. of iron phthalocyanine were warmed to 70° in a boiling-tube carrying a long air-condenser and an inlet for air or oxygen. After 36 hrs., the deep brown product, which no longer contained phthalocyanine, was distilled in a vacuum. A low-boiling fraction of recovered octalin with some ketone was discarded (3·70 g.), and Δ^2-*α-octalone* was collected at 114°/5 mm. (3·15 g.). A small high-boiling fraction was not examined. Redistillation of the ketonic fraction yielded the pure octalone as a colourless unsaturated liquid, which however gave no distinctive colour with ferric chloride (Found : C, 79·8; H, 9·5. $C_{10}H_{14}O$ requires C, 80·0; H, 9·3%). The *semicarbazone* was prepared by adding 0·7 g. of the ketone to a hot solution of 0·7 g. of semicarbazide hydrochloride in a mixture of 25 c.c. of water, 20 c.c. of alcohol, and 7 c.c. of saturated sodium acetate; it separated on cooling (1·15 g.), and after twice crystallising from alcohol melted sharply at 203—204° (Found : C, 64·05; H, 7·95. $C_{11}H_{17}ON_3$ requires C, 63·8; H, 8·2%).

500 Mg. of Δ^2-α-octalone were shaken in an atmosphere of hydrogen in 25 c.c. of alcohol containing 300 mg. of 10% palladium–charcoal. After 36 mins., when 1 mol. of hydrogen had been absorbed, reduction was interrupted, the filtered solution concentrated, and the ketone converted directly into an impure semicarbazone, m. p. 200—205°, raised by five crystallisations to 229°; mixed m. p. with authentic *trans*-α-decalonesemicarbazone, 229°.

Oxidation of α-Pinene.—The method was similar to that employed with other hydrocarbons (8 g. of *d*-α-pinene, 45 mg. of iron phthalocyanine; 4 days at 70° in oxygen). The product was distilled in steam, the readily volatile unattacked pinene rejected, and the more difficultly volatile oxidation products collected. The oily distillate was treated in the hot with excess of semicarbazide hydrochloride and sodium acetate, and a very small quantity of semicarbazone, m. p. 207°, collected after 3 days (the optically active forms of verbenonesemicarbazone have m. p. 208—209°). The non-ketonic oil from the semicarbazide preparation yielded a fraction, b. p. 110—115°/16 mm. (verbenol).

Oxidation of cyclo*Hexene.*—The following experiments illustrate the ability of iron phthalocyanine to promote the absorption of oxygen by this compound. 10 G. of *cyclo*hexene, dissolved in 10 g. of acetone, were shaken in oxygen (*a*) without additional catalyst and (*b*) with 100 mg. of iron phthalocyanine. The absorption of oxygen in (*a*) during 18 hrs. was 40 c.c., and in (*b*) it was as follows :

Time, mins.	5	8	21	27	50	2880
Uptake of oxygen, c.c.	27·5	37·5	60·0	73·0	118·5	1550

The limiting value (1550 c.c. measured at 20° and 765 mm. over water = 1420 c.c. at *N.T.P.*) is somewhat in excess of that required for one atom of oxygen per molecule of *cyclo*hexene. Distillation yielded, however, a moderate recovery of *cyclo*hexene, and 4·1 g. of its peroxide as an oil with a very pungent odour, and which decomposed in contact with iron phthalocyanine.

Oxidation was also effected as with the other hydrocarbons (100 g. of *cyclo*hexene treated with oxygen at 70° for 4 days in presence of 100 mg. of iron phthalocyanine). Direct distillation of the product without preliminary separation of the catalyst gave 61 g. of *cyclo*hexene. At 140° mild decomposition set in, and a further 11·5 g. of oxidation product subsequently distilled (b. p. 160—170°). Redistilled, it had b. p. 166° and agreed in properties with Δ^1-*cyclo*hexen-3-ol (Willstätter and Sonnenfeld, *loc. cit.*).

Oxidation of Δ^1*-Methyl*cyclo*hexene.*—50 G. of this compound were oxidised as before in an atmosphere of oxygen at 70° in presence of 20 mg. of iron phthalocyanine. Simple distillation after 72 hrs. yielded 5·7 g. of recovered hydrocarbon and 24·1 g. of a fraction, b. p. 55—80°/5 mm.; 4·8 g. of a thick colourless oil, b. p. 130°/5 mm., were also obtained. The large intermediate fraction was a mixture of ketone and alcohol, which was only partly separated on further fractionation, but was converted completely into ketone (b. p. 76—78°/17 mm.) on oxidation with a limited amount of acid dichromate in the normal manner. The ketonic product is almost if not exclusively pure Δ^1-methyl*cyclo*hexen-3-one, as more drastic oxidation with chromic acid yielded only succinic acid and no detectable trace of glutaric acid (cf. Hagemann, *Ber.*, 1893, **26**, 886). The semicarbazone after three crystallisations from alcohol had m. p. 196—198° (Vorländer and Gärtner, *Annalen*, 1898, **304**, 23, give m. p. 199—201°) (Found : N, 24·75. Calc. for $C_8H_{13}ON_3$: N, 25·15%). Δ^1*-Methyl*cyclo*hexen-3-one-2 : 4-dinitrophenylhydrazone* had m. p. 150° (from alcohol) (Found : C, 54·2; H, 4·82; N, 19·0. $C_{13}H_{14}O_4N_4$ requires C, 53·9; H, 4·83; N, 19·3%).

Oxidation of Diphenylmethane.—A suspension of 20 mg. of iron phthalocyanine in 7·5 g. of diphenylmethane was maintained for 30 hrs. at 110° whilst a slow stream of oxygen was passed in. Distillation of the product in a vacuum yielded 4·6 g. of unchanged diphenylmethane

(b. p. 125°/1 mm.), a very small intermediate fraction, and 2·2 g. of benzophenone (b. p. 146°/1 mm., m. p. 48°, m. p. and mixed m. p. of the 2 : 4-dinitrophenylhydrazone with an authentic specimen, 238°), only a very small residue remaining.

Oxidation of Cholesteryl Acetate.—2 G. of the acetate were treated with oxygen for 42 hrs. in 10 c.c. of xylene at 100° containing 20 mg. of iron phthalocyanine (which dissolved to a clear blue-green solution). The resulting brown liquid was diluted to 50 c.c. with benzene, filtered through a 20-cm. column of activated alumina (2·0 cm. diam.), and the chromatogram washed with a further 150 c.c. of benzene. The fractions eluted from the chromatogram with benzene–methanol (2 : 1) furnished only non-crystallising gums : Upper zone (brown, 5 cm.), eluate 200 mg.; intermediate zone (red, 2 cm.), eluate, 300 mg.; lower zone (light brown, 13 cm.), eluate, 590 mg. The filtrate was evaporated in a vacuum and stirred with 5 c.c. of methylated spirit to precipitate 175 mg. of 7-ketocholesteryl acetate, m. p. and mixed m. p. with an authentic specimen prepared by oxidising cholesteryl acetate with chromic acid, 153°. Neither cholesterol itself nor its dihydrogen phosphoric ester (v. Euler, Wolff, and Hellstrom, *Ber.*, 1929, 62, 2455) was affected by the above treatment.

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