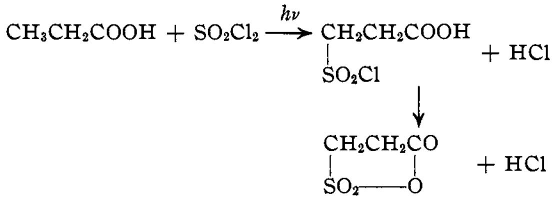
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Sulfonation Reactions with Sulfuryl Chloride. II. The Photochemical Sulfonation of Aliphatic Acids with Sulfuryl Chloride

BY M. S. KHARASCH, T. H. CHAO[1] AND HERBERT C. BROWN

Until recently, the use of sulfuryl chloride as a sulfonating agent has been restricted to the sulfonation of aromatic hydrocarbons with the aid of aluminum chloride.[2] The discovery that saturated hydrocarbons can be sulfonated directly by sulfuryl chloride with the aid of light[3] suggests a new approach to the preparation of sulfoparaffins and their derivatives.

The sulfonation of paraffinic and cycloparaffinic hydrocarbons by this method requires the presence of a small quantity of a catalyst (pyridine is especially effective) in the reaction mixture. On the other hand, the photochemical sulfonation of aliphatic acids can be effected readily in the absence of an added catalyst.[4] Furthermore, the product formed in the sulfonation of hydrocarbons is the alkyl sulfonyl chloride, while the product isolated from the sulfonation of the lower members of the aliphatic acids is a cyclic sulfoanhydride.[5]



$$\mathrm{CH_3CH_2COOH} + \mathrm{SO_2Cl_2} \xrightarrow{h\nu} \begin{array}{l}\mathrm{CH_2CH_2COOH}\\ | \\ \mathrm{SO_2Cl}\end{array} + \mathrm{HCl}$$

$$\downarrow$$

$$\begin{array}{l}\mathrm{CH_2CH_2CO}\\ | \qquad\quad | \\ \mathrm{SO_2}\text{——}\mathrm{O}\end{array} + \mathrm{HCl}$$

In the present paper we are reporting the results of our study of the sulfonation of a number of aliphatic acids, and the behavior of this new class of substances (*i. e.*, the inner anhydrides of the aliphatic sulfocarboxylic acids) toward a variety of chemical reagents.

Photochemical Sulfonation of Aliphatic Acids.—The best results in the photochemical sulfonation of the lower aliphatic acids were obtained by slow addition of a slight excess of the sulfuryl chloride to the reaction flask containing the aliphatic acid. The temperature of the reaction mixture was kept at 50–60°; illumination was furnished by an ordinary incandescent lamp (200–300 watts). After the reaction had gone to completion (three to four hours), ligroin was added to the reaction mixture to precipitate the sulfocarboxylic acid anhydrides.

It is significant that in every case which we have investigated, the sulfonated products consisted of the beta or beta and gamma derivatives. In no case have we been able to demonstrate the formation of the alpha substituted isomer. On the other hand, the chlorinated acids which are formed simultaneously (in somewhat smaller amounts) were largely the alpha substituted derivatives.

Acetic acid cannot be sulfonated by this procedure. The only products we have isolated from the action of sulfuryl chloride upon this acid were the chlorinated derivatives.

With this exception, all other aliphatic acids we have investigated undergo sulfonation with ease. Propionic acid was sulfonated to form the cyclic anhydride of β-sulfopropionic acid in a yield of 52%. The anhydride is a white crystalline solid which melts sharply at 76–77°; it is readily transformed by hydration into β-sulfopropionic acid which is also a crystalline solid, melting at 102–103°. The absence of any appreciable amount of alpha sulfonated propionic acid in the product was demonstrated by a careful examination of the barium salt of the sulfoacid.[4]

Isobutyric acid is sulfonated with ease and the yield of the sulfoanhydride is good. In this case the product formed is an oil. The hydrated product, which is also an oil, was identified as a sulfobutyric acid by its neutralization equivalent and the analysis of its barium salt. Both the free acid and its derivatives appear to be homogeneous. Since their properties differ markedly from those reported for α-sulfoisobutyric acid and its corresponding derivatives, we have concluded that the sulfo group must be in the beta position.

The product obtained from the sulfonation of *n*-butyric acid is probably a mixture of the cyclic anhydrides derived from the corresponding β- and γ-sulfobutyric acids. We have not separated the individual components of the reaction product.

The sulfonation of isovaleric, hexahydrobenzoic

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[1] Eli Lilly Fellow, 1939–1940.

[2] Böeseken, *Rec. trav. chim.*, **30**, 381 (1911).

[3] Kharasch and Read, THIS JOURNAL, **61**, 3089 (1939).

[4] Kharasch and Brown, *ibid.*, **62**, 925 (1940).

[5] This product is obtained only if the reagents used are carefully dried and every precaution is taken to exclude moisture. Otherwise, the product which is isolated is the corresponding sulfocarboxylic acid.

and lauric aids was studied. Because of the large number of possible isomers, we have not investigated these products in detail, except to demonstrate that large quantities of sulfonyl chlorides were present, indicative that positions other than beta and gamma (and therefore not favorable for cyclization and anhydride formation) were substituted.

Mechanism of Photochemical Sulfonation.—The mechanism we wish to suggest for this photosulfonation reaction is

$$SO_2Cl_2 \xrightarrow{\text{pyridine}} SO_2 + Cl_2 \qquad (1)$$

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \qquad (2)$$

$$Cl\cdot + RH \longrightarrow R\cdot + HCl \qquad (3)$$

$$R\cdot + SO_2 \longrightarrow RSO_2\cdot \qquad (4)$$

$$RSO_2\cdot + Cl_2 \longrightarrow RSO_2Cl + Cl\cdot \qquad (5)$$

It is obvious that a satisfactory mechanism for the photochemical sulfonation reaction must explain plausibly why the use of peroxides either in the dark or in the light yields only chlorinated derivatives, while the use of pyridine or thiophenol or the other sulfonation catalysts yields *both* sulfonated and chlorinated derivatives in varying relative amounts.[3] A significant clue is furnished by the observation that the reaction mixture containing the peroxide catalyst remains colorless, water-clear, from start to end of the preparation. On the other hand, the addition of a sulfonation catalyst is followed immediately by the appearance of the greenish-yellow color of chlorine. This may be taken as definite experimental support for the reaction as postulated in step (1). Steps (2) and (3) in the mechanism require no elaboration.

The organic radical formed in step (3) may undergo in solution the following changes

$$R\cdot + SO_2Cl_2 \longrightarrow RCl + \cdot SO_2Cl \qquad (a)$$

$$R\cdot + Cl_2 \longrightarrow RCl + \cdot Cl \qquad (b)$$

$$R\cdot + SO_2 \longrightarrow RSO_2\cdot \qquad (c)$$

Of these three possibilities, reaction (a) will require the highest energy of activation, reaction (b) will require somewhat less and should therefore proceed more readily, while reaction (c) should require little or no energy of activation (since no bond is broken) and this reaction should be most favored.

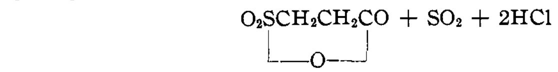
The resulting free radical, $RSO_2\cdot$, can dissociate, reversing the reaction; or it can stabilize itself by reacting with chlorine as in (5). We must postulate that this $RSO_2\cdot$ free radical cannot react with sulfuryl chloride at any appreciable rate since, in the peroxide-catalyzed reaction, in which both substances must be present, no measurable quantity of sulfonated products is formed. We are therefore led to the conclusion that it is the presence of free chlorine in the reaction mixture which directs the course of the reaction toward the formation of the alkyl sulfonyl chloride.

Strong support for this mechanism is the fact that a mixture of sulfur dioxide and chlorine in the presence of light reacts with paraffinic hydrocarbons to form sulfonyl chloride derivatives.[6]

These considerations suggest experimental conditions favoring high yields, for it follows that the peroxide-catalyzed chlorination reaction should proceed best if the reaction mixture is kept boiling vigorously, while in the sulfonation reaction, boiling the reaction mixture should greatly decrease the yield. These conclusions have been verified.

The exclusive sulfonation of the beta carbon atoms in the case of propionic and isobutyric acids deserves some comment, particularly if the chain reaction is assumed to be propagated by chlorine atoms. It is our opinion that the alpha sulfonyl chlorides of the acids are formed momentarily, but since they cannot stabilize themselves by anhydride formation, they decompose into the alpha chloroacids and sulfur dioxide. These deductions are in agreement with the results obtained in the sulfonation and chlorination of propionic acid for which accurate data are available. The yield of α-chloropropionic acid is the same in both cases (45%) but in the sulfonation reaction instead of 55% of the beta chloro derivative a corresponding amount of the sulfonated compound is produced. The same explanation accounts for the formation of the alpha chlorinated and beta sulfonated derivatives in the photochemical sulfonation of ethylbenzene with sulfuryl chloride.[3,7]

The Cyclic Anhydrides of Aliphatic Sulfocarboxylic Acids.—The cyclic aliphatic sulfoanhydrides can be obtained readily by means of the reaction described in this paper or can be prepared from the corresponding sulfoacids by treatment with thionyl chloride.



$$HO_3SCH_2CH_2COOH + SOCl_2 \longrightarrow \underbrace{O_2SCH_2CH_2CO}_{\text{—O—}} + SO_2 + 2HCl$$

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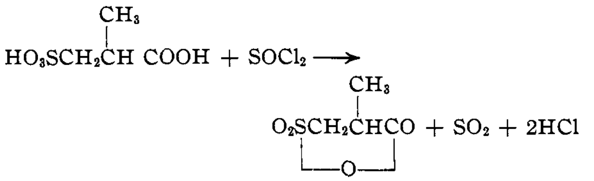
[6] Kharasch and Alsop, unpublished work; Reed, U. S. Patent 2,046,090.

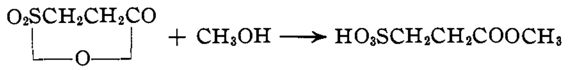
[7] Kharasch, May and Mayo, *J. Org. Chem.*, **3**, 189 (1938).



$$HO_3SCH_2\overset{CH_3}{\overset{|}{C}}H\,COOH + SOCl_2 \longrightarrow \underbrace{O_2SCH_2\overset{CH_3}{\overset{|}{C}}HCO}_{O} + SO_2 + 2HCl$$

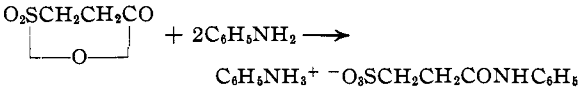
The monomeric formulas for these inner anhydrides are derived from molecular weight determinations.

The reactions of these inner anhydrides are similar to those of their previously known aromatic homolog, the inner anhydride of *o*-sulfobenzoic acid. For example, the inner anhydride of β-sulfopropionic acid reacts with methyl alcohol to form the monomethyl ester, a solid of melting point 73°. The measurement of the *p*H of solutions of this ester of known concentrations indicated a high degree of dissociation, calculated as a monobasic acid, and established that esterification involves the carboxylic acid group. The reaction is



$$\underbrace{O_2SCH_2CH_2CO}_{O} + CH_3OH \longrightarrow HO_3SCH_2CH_2COOCH_3$$

Treatment of the anhydride with aniline yields the aniline salt of the sulfoacid anilide.



$$\underbrace{O_2SCH_2CH_2CO}_{O} + 2C_6H_5NH_2 \longrightarrow C_6H_5NH_3^+ \ {}^-O_3SCH_2CH_2CONHC_6H_5$$

Similarly, treatment with ammonia yields the corresponding ammonium salt of the carboxylic acid amide. The position of the anilide and amide groups in these substances was established by a method similar to that used to establish the structure of the monomethyl ester.

Experimental Part

General Procedure for the Photochemical Sulfonation of the Aliphatic Acids.—The acid and excess sulfuryl chloride (molar ratio 1:1.375) is placed in a round-bottomed flask attached to an efficient reflux condenser by means of a ground-glass joint. The flask is illuminated by a tungsten filament lamp (200–300 watts) placed near the flask. The temperature range 50–60° has been found to be the optimum for this reaction.

Under these conditions, the reaction involving one mole of organic acid and one mole of sulfuryl chloride is complete in from three to six hours. The end of the reaction is indicated when the evolution of gases ceases. A mixture of low boiling ligroin and benzene (80:20) is then added to the contents of the reaction flask. The sulfonated product separates. It is collected on a filter, washed several times with dry ligroin and dried in a vacuum desiccator.

Higher temperatures of sulfonation decrease the yield. The addition of pyridine as a catalyst exerts no noticeable effect upon the sulfonation of the lower aliphatic acids, such as propionic and butyric acids, but it definitely aids the sulfonation of the higher aliphatic acids. The slow addition of sulfuryl chloride during the course of the reaction increases slightly the conversion of the acid over that obtained when the reagents are mixed at the start of the reaction. However, the increase in yield is small.

Sulfonation of Propionic Acid.—A mixture of 74 g. of anhydrous propionic acid (1.0 mole) and 185.6 g. of sulfuryl chloride (1.375 mole) was placed in a flask and treated as described in the general procedure. As the reaction proceeded, a white solid separated. Although the reaction appeared to be complete in five hours, illumination was continued for several hours longer. Dissolved gaseous products and excess sulfuryl chloride were removed under reduced pressure and the ligroin–benzene mixture (200 cc.) added to complete the separation of the solid and to facilitate filtration. The precipitate was collected on a Büchner funnel, moisture being carefully excluded, and washed with small portions of dry ligroin. When dried *in vacuo* in a desiccator containing fused sodium hydroxide, phosphorus pentoxide and paraffin wax, it weighed 58 g. The ligroin–benzene filtrate was fractionated and 13 g. of unreacted propionic acid and 40 g. of chloropropionic acid were obtained.

The identification of the product obtained in this reaction as the cyclic anhydride of β-sulfopropionic acid was accomplished by analysis and by hydration into β-sulfo-

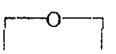
TABLE I

PHOTOCHEMICAL SULFONATION OF ORGANIC ACIDS

Acid treated[a]	Catalyst[b]	Temp., °C.	Conversion, %	Cl acid, %	Sulfoacid, %	Remarks
Propionic	o	Reflux	46	64	37	[c]
Propionic	o	50–60	76	21	65	[c]
Propionic	o	50–60	89	32	57	C_6H_6 as solvent: mole fraction of C_6H_6 = 50%
Propionic	o	50–60	100	32	54	[d]
Propionic	py	50–60	90	20	60	[d]
Lauric	py	50–60	..	..	60	[c] 40 ml. CCl_4 as solvent
Lauric	o	50–60	..	..	Bound S, trace	[c] 40 ml. CCl_4 as solvent
n-Butyric	o	50–60	94	8	55	[d]
n-Butyric	py	50–60	89	9	67	[d]
Isobutyric	py	50–60	70	28	42	[d]

[a] In all experiments 0.2 mole acid and 0.275 mole sulfuryl chloride was used. [b] py = 4 drops of pyridine. [c] SO_2Cl_2 and acid were mixed at beginning of experiment. [d] SO_2Cl_2 added dropwise.

propionic acid. The anhydride, isolated directly from the reaction mixture as described above, appears to be analytically pure. The melting point of this material was 76–77° and it was not changed by crystallization from either benzene or thionyl chloride.



Anal. Calcd. for $C_3H_4O_4S(O_2SCH_2CH_2CO)$: S, 23.5; neut. equiv., 68.0; mol. wt., 136. Found: S, 23.3; neut. equiv., 67.5; mol. wt. (Rast method), 147.

Sulfonation of Isobutyric Acid.—From a reaction mixture consisting of 0.2 mole isobutyric acid and 0.275 mole sulfuryl chloride there was isolated α-chloroisobutyric acid in yield of 28% and the inner anhydride of β-sulfoisobutyric acid in yield of 42%. The conversion was 70%.

The sulfoanhydride obtained from isobutyric acid separates from the reaction mixture after addition of the ligroin–benzene diluent as an oil. It may be distilled at low pressures with but slight decomposition (b. p. 135–145° at 3 to 5 mm.; $d^{22.5}$ 1.442).

Anal. Calcd. for $C_4H_6O_4S$: S, 21.3; neut. equiv., 75.0. Found: S, 21.1; neut. equiv., 76.2.

The assignment of the sulfo group to the beta position is based on a comparison of the approximate solubilities of the barium salts of this compound (42.2% at 26°) with that of the barium salt of a known α-sulfoisobutyric acid (12.1% at 26°).

Sulfonation of *n*-Butyric Acid.—The sulfoanhydride obtained from the sulfonation of *n*-butyric acid is an oil. The product which is probably a mixture of the beta and gamma sulfonated derivatives, cannot be distilled without extensive decomposition. The oil was washed with small portions of ligroin and then dried *in vacuo*.

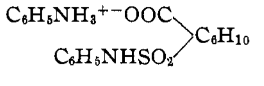
Anal. Calcd. for $C_4H_6O_4S$: neut. equiv., 75.0. Found: neut. equiv., 74.4.

The product was identified as a sulfonated derivative of *n*-butyric acid by the analysis of some crystalline derivatives described in a later section.

Sulfonation of Isovaleric, Hexahydrobenzoic and Lauric Acids.—In the sulfonation of these acids, the addition of a small quantity of pyridine (4 drops) to the reaction mixture increases the yields. Because of the large numbers of isomers and the great difficulty of working with these sulfonated derivatives, no attempt was made to isolate the individual sulfonated acids. The presence of sulfochloride groups in the product (indicative of sulfonation in positions other than beta and gamma) was demonstrated by the reaction with aniline.

The yields were calculated by analysis for sulfur of the residue after removal of the volatile constituents from the reaction mixture. In each of these three acids yields of sulfonated derivatives of from 25 to 60% were indicated.

The procedures used in these studies may be illustrated by a consideration of the sulfonation of hexahydrobenzoic acid. Six grams of the residue, freed of all volatile material, was treated with excess aniline. There was obtained 2.3 g. of the aniline salt of the sulfoanilide



and approximately 75% of the calculated quantity of chlorine was liberated as chloride ions according to the reaction

$$R{-}SO_2Cl + 2C_6H_5NH_2 \longrightarrow R{-}SO_2NHC_6H_5 + C_6H_5NH_3^+Cl^-$$

Anal. Calcd. for $C_6H_{10}(SO_2NHC_6H_5)(COO^-NH_3^+{-}C_6H_5)$[8]: S, 8.52. Found: S, 8.80.

The Cyclic Anhydrides of Aliphatic Sulfocarboxylic Acids.—The physical properties of the cyclic anhydrides of sulfopropionic, sulfoisobutyric and sulfo-*n*-butyric acids have been described. These anhydrides react readily with water to form the corresponding sulfoacids; these acids may be reconverted into the anhydrides by treatment with thionyl chloride.

The anhydrides react readily with alcohols, ammonia and amines. Some of these derivatives are crystalline substances which may be used for the identification of the anhydrides.

Reaction with Aniline.—An excess of aniline dissolved in benzene was treated with β-sulfopropionic anhydride. A vigorous reaction ensued and a white solid separated. This solid was crystallized from hot water. It melted sharply at 216°. Addition of cold dilute sodium hydroxide liberates aniline, indicating that at least part of the aniline was bound in the form of a salt. The solution in water was sufficiently acid so that it could be titrated with sodium hydroxide to a sharp end-point using phenolphthalein as indicator.

Anal. Calcd. for $C_{15}H_{15}O_4N_2S(C_6H_5NH_3^{+\,-}O_3SCH_2CH_2CONHC_6H_5)$: N, 8.71; neut. equiv., 322. Found: N, 8.62; neut. equiv., 320.

The fact that the compound can be titrated to a sharp end-point indicates that it must be the sulfonic acid group which is involved in the salt formation and the carboxylic acid group which is bound in the form of an anilide. In order to establish this point a solution of the salt of known concentration was treated with the theoretical quantity of barium hydroxide. The aniline set free was extracted from the mixture with benzene. To the aqueous solution thus obtained there was added the calculated quantity of sulfuric acid. The barium sulfate was removed by filtration. The resulting solution of the anilide was diluted to 0.02 *N* and the *p*H determined. The value obtained, 2.08, is close to that obtained for a 0.02 *N* solution of β-sulfopropionic acid itself, 1.99, and thus establishes that the sulfonic acid group must be free and the structure of the salt must be $C_6H_5NH_3^+O_3^-SCH_2CH_2CONHC_6H_5$.

β-Sulfoisobutyric anhydride reacts to form a similar crystalline derivative which decomposes sharply at 238°.

Anal. Calcd. for $C_{16}H_{20}O_4N_2S$: N, 8.33; neut. equiv., 336. Found: N, 8.25; neut. equiv., 329.

A similar product was obtained from sulfo-*n*-butyric anhydride. This material melted over a wide range; it appears to be a mixture of isomers.

Anal. Calcd. for $C_{16}H_{20}O_4N_2S$: neut. equiv., 336. Found: neut. equiv., 340.

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(8) The evidence for the structure assigned, *i. e.*, with the sulfo groups united with the anilide group, is the observation that the substance cannot be titrated with sodium hydroxide to a sharp end-point. The aniline salt of a sulfonic acid can be titrated with ease (see below).

Reaction with Ammonia.—β-Sulfopropionic anhydride was added in small portions to a large excess of liquid ammonia. After removal of the ammonia by evaporation, the white crystalline material was warmed gently to 60° to remove the last traces of ammonia and crystallized from 80% methanol. The crystallized product melted at 179°. It was identified as the ammonium salt of β-sulfopropionamide by its reactions and analysis.

Anal. Calcd. for $C_3H_{10}O_4H_2S$ ($NH_4^{+-}O_3SCH_2CH_2CONH_2$): N, 16.45. Found: N, 16.50.

Reaction with Methyl Alcohol.—β-Sulfopropionic anhydride was treated with a slight excess of anhydrous methanol and the excess then removed in a vacuum desiccator over phosphorus pentoxide. A crystalline highly hygroscopic material was obtained. The melting point of this substance was 73°.

Anal. Calcd. for $C_4H_8O_5S$ ($HO_3SCH_2CH_2COOCH_3$): S, 19.1; neut. equiv., 168. Found: S, 18.9; neut. equiv., 162.

Proof that the carboxylic acid group is esterified in this molecule and the sulfonic acid group is free was established in a manner similar to that described for the anilide. A 0.02 *N* solution of the ester was prepared and the *p*H determined immediately.[9] The value obtained, 2.05, indicates that the free acid group is highly ionized. It is concluded therefore that the sulfonic acid group must be free.

Summary

1. Sulfuryl chloride reacts with aliphatic carboxylic acids in the presence of actinic light to yield sulfonated derivatives.

2. The lower aliphatic acids (propionic, isobutyric, butyric) yield cyclic sulfocarboxylic anhydrides in which the sulfo groups are in the beta or beta and gamma positions, while the higher aliphatic acids (valeric, hexahydrobenzoic, lauric) yield sulfonyl chlorides indicative of substitution in positions other than beta and gamma.

3. The reactions of the sulfoacid anhydrides with alcohols, ammonia and amines have been investigated.

4. A chain mechanism involving chlorine atoms and organic free radicals is suggested to explain the photochemical sulfonation of aliphatic compounds.

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[9] The ester hydrolyzes rather rapidly in aqueous solution.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA]

Preparation and Properties of Derivatives of Inositol*

BY FOREST A. HOGLAN AND EDWARD BARTOW

Hoglan and Bartow[1] prepared inositol in large quantities cheaply from calcium phytate, the precipitate made by adding lime to starch factory steep water. They used hydrolysis without acid or alkali and obtained 9 to 12 lb. of inositol for each 100 lb. of starting material.

Having made several new esters of inositol,[1] the authors have continued the study of inositol and derivatives.

Experimental Procedure

Preparation of Inositol.—Better calcium phytate was obtained from light steep water than from heavy steep water. To determine which was the better, calcium phytate was precipitated from both light and heavy steep water and each was treated as described by Bartow and Walker[2] except that hydrolysis was carried out in three shallow metal containers instead of 21 jars. These containers, each 60 cm. deep, were made from 30 gallon (190 liter) gasoline drums by cutting out the center portion and using the ends as containers. These containers eliminated excessive handling, obviated any loss of material due to breakage, and yet provided the uniform heat distribution required for hydrolysis. In each experiment about 225 kg. of the wet precipitate, which was equivalent to about 40 kg. of dry phytin, was hydrolyzed by heating in an autoclave for ten hours under 5.6 sq. cm. steam gage pressure. 9.5% of inositol was obtained from the light steep water precipitate and 8.1% from the heavy steep water precipitate. The light steep water precipitate gave a product of higher purity. The inositol obtained from heavy steep water precipitate contained considerable protein material and was very difficult to purify.

Oxidation of Inositol with Nitric Acid.—Previous investigators[2,3,4] have oxidized inositol with concentrated or fuming nitric acid, dried the oxidized product until free from nitric acid, and neutralized a water solution of the oxidized product with sodium bicarbonate or potassium bicarbonate, obtaining salts of tetrahydroxyquinone, green crystalline compounds. By neutralizing with sodium and potassium carbonates, they obtained violet colored crystalline compounds which they called rhodizonates. The authors have thus far been unable to distinguish tetrahydroxyquinone from rhodizonic acid.

Inositol has been oxidized under various conditions and various concentrations of nitric acid and the products have been used in the preparation and study of derivatives.

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* Original manuscript received August 3, 1939.

[1] F. Hoglan and E. Bartow, *Ind. Eng. Chem.*, **31**, 749–750 (1939).

[2] E. Bartow and W. W. Walker, *ibid.*, **30**, 300–303 (1938).

[3] O. Gelormini and N. Artz, THIS JOURNAL, **52**, 2483 (1930).

[4] M. Maquenne, *Compt. rend.*, **104**, 297 (1887).