

An experiment carried out with 3 g. of 1,2-benzylidene glycerol, similarly treated with dry hydrogen chloride but without any preliminary heating and allowed to stand for one month at room temperature, yielded 0.45 g. of 1,3-benzylidene glycerol.

### Summary

1. The preparation, isolation, quantitative separation and inter-conversion of the isomeric 1,2- and 1,3-benzylidene glycerols are described.

2. The corresponding methyl ethers have been prepared and their physical constants determined.

3. The remarkably labile character of the oxygen ring is shown by the ease of partial transformation of either of the acetals into the corresponding isomer at a low temperature under the influence of traces of gaseous hydrochloric acid. The bearing of this on polysaccharide investigations is pointed out.

4. Glycerol  $\beta$ -methyl ether has been isolated for the first time in a pure state. It is apparently the first pure  $\beta$ -derivative of glycerol to be reported in the literature.

MONTREAL, CANADA

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[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY,  
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## STUDIES ON THE REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES.

### XVI. SEPARATION AND IDENTIFICATION OF THE ISOMERIC ETHYLIDENE GLYCEROLS<sup>1</sup>

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The importance of the cyclic acetal and ketal glycerols has long attracted the interest of investigators in the field of carbohydrate chemistry. Such workers as Tollens,<sup>5</sup> Fischer,<sup>6</sup> Karrer,<sup>7</sup> Irvine,<sup>8</sup> and more recently

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<sup>4</sup> This paper represents the second of a forthcoming series of publications carried out under the joint auspices of the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their keen appreciation of the generous facilities placed at their disposal by the three coöperating agencies.

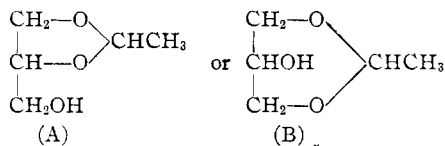
<sup>5</sup> Schulz and Tollens, *Ann.*, **289**, 29 (1896).

<sup>6</sup> Fischer, *Ber.*, **27**, 1536 (1897).

<sup>7</sup> Karrer, *Helv. Chim. Acta*, **4**, 728 (1921).

<sup>8</sup> Irvine, Macdonald and Soutar, *J. Chem. Soc.*, **107**, 337 (1915).

Hibbert and his pupils<sup>9</sup> have studied or used this class of compounds in their efforts to explain, by analogy, certain features of the chemical behavior of the more complex polysaccharides. It is remarkable, therefore, that up to the present time the molecular structure of one of the simplest glycerol acetals, namely, ethylidene glycerol, has remained undetermined, its formula being given as either, or both, of the two possible isomeric forms



Schulz and Tollens,<sup>5</sup> working with the lower homolog, methylidene glycerol, indicated the existence of both of the corresponding isomeric forms since, under different experimental conditions, they were able to obtain products which, in one case, yielded a benzoate as a crystalline product, in the other as an oil. The isomers were not identified, however, and the method used in their preparation left some doubt as to their existence as different chemical individuals.<sup>9a</sup>

With respect to the structure of ethylidene glycerol, however, there has been no evidence brought forward as to which of the two forms, A or B, should be assigned as its molecular constitution. This is due in large part to the extreme ease of hydrolysis of this product and the consequent difficulty of obtaining any derivative not involving rupture of the acetal ring.

Ethylidene glycerol was first prepared by Harnitzky and Menschutkine<sup>10</sup> and later, in much purer form, by Nef,<sup>11</sup> the formula being given as either A or B.

Recent work<sup>12</sup> has shown that in benzaldehyde condensations with glycerol a "partition" occurs, both the five and the six membered cyclic acetals being formed simultaneously. In view of these results, as well as those from earlier experiments in this field,<sup>9</sup> it was concluded that ethylidene glycerol would also prove to be a mixture of the two ring systems (A) and (B). The present investigation deals with the separation and identification of these isomers, and of several of their derivatives.

The isomeric ethylidene glycerols are obtained as a mixture in either of the two recognized methods of preparation.<sup>9</sup> The crude product in both

<sup>9</sup> Hill and Hibbert, *THIS JOURNAL*, **45**, 3121 (1923).

<sup>9a</sup> Neal Carter has recently succeeded in isolating and identifying the two pure methylidene glycerols and their corresponding benzoates. An account of this work is to be published in the immediate future. (H. H.)

<sup>10</sup> Harnitzky and Menschutkine, *Ann.*, **136**, 126 (1865).

<sup>11</sup> Nef, *Ann.*, **335**, 216 (1904).

<sup>12</sup> Hill, Whelen and Hibbert, *THIS JOURNAL*, **50**, 2235 (1928).

cases boils at 176–187° (760 mm.), the rise in temperature during distillation, even with a fractionating column, being very gradual. Operating under reduced pressure, however, it is possible, by several fractionations, to obtain two distinct products, Fraction I, b. p. 86–88° (21 mm.), and Fraction II, b. p. 101–103.5° (20 mm.), neither of which, however, can be considered as a pure material.

The acetylene method of preparation yielded the sharpest boiling low fraction, while that from the paraldehyde method gave the most definite high boiling product. From this observation it would appear that the partition between the two isomeric forms of ethylidene glycerol may vary considerably, according to the method and conditions of preparation.

The fractions from either method have the same percentage composition and each, upon hydrolysis with dilute phosphoric acid, yields the same theoretical amount of acetaldehyde. Differences in the densities and refractive indices, however, further indicate the presence of isomers.

Many unsuccessful attempts were then made, using the low boiling fraction from the acetylene method and the high boiling from the paraldehyde process (as representing the purest samples), to isolate an acylated product, and this was finally achieved by the use of benzoyl chloride in dry pyridine solution. This reagent causes no hydrolysis of the acetal ring and readily yields two well defined glycerol-acetal-benzoates, that from the low boiling fraction being crystalline (m. p. 86°) and that from the high boiling product an oil, b. p. 163 (11 mm.).

The isolation of these benzoates in a pure state proved to be the key to this research, especially since a fortunate difference in solubility in ligroin permitted of an almost quantitative separation.

Employing the mixture of isomers obtained by the acetylene method, benzoylating the product and separating the mixed benzoates by the use of cold ligroin, it was possible to isolate the isomeric benzoates, the ratio of the amounts of the crystalline to the liquid form being 1:1.8. This ratio may be regarded as an approximately accurate value of the extent of the partition between the low and high boiling ethylidene glycerols, respectively, as prepared by this method.

Applying the same procedure to the mixture of ethylidene glycerols obtained from the reaction of paraldehyde with glycerol, the relative amounts of the low and high boiling isomers were found to be 1:4.

Two conclusions may be drawn from these partitions. 1. The formation of the high boiling isomer—later shown to have the five membered cyclic configuration (A)—is definitely favored over that of the six membered derivative (B). 2. The partition ratio is a variable one, the relative amounts of each isomer formed depending on experimental conditions such as temperature, concentration of acid, etc. There is no reason to suppose that the actual mechanism of ring closure is any different in the

preparation from acetylene than from paraldehyde. Furthermore, it is to be expected, as found in the preceding paper<sup>12</sup> (Part XV) on the isomeric benzylidene glycerols that under standard conditions, there will always exist a final equilibrium mixture which should be the same irrespective of whether this is approached from the side of the five or from that of the six membered acetal.

**Structural Identification of the Isomers.**—Since the isomeric ethylidene glycerol benzoates may thus be separated and isolated in a pure condition, these derivatives were used as the starting point to determine the structure of the original acetals. It was found possible to hydrolyze off the benzoyl group, leaving the acetal ring intact.

In this way, starting with the pure benzoates, two isomeric ethylidene glycerols were obtained for the first time, as pure individual compounds.

The structures of these acetals were determined essentially as in the case of the benzylidene glycerols, namely, by the methylation-hydrolysis method developed by Irvine and co-workers. Silver oxide and methyl iodide was used as the methylating agent, since Haworth's methyl sulfate method proved unsatisfactory.

Each of the two ethylidene glycerols yielded an isomeric ethylidene glycerol methyl ether which, in turn, on hydrolysis, gave an isomeric glycerol monomethyl ether.

The low boiling ethylidene glycerol (purified through its crystalline benzoate) gave only glycerol  $\beta$ -methyl ether, identical with that isolated for the first time from 1,3-benzylidene glycerol, while the higher boiling ethylidene glycerol (from its liquid benzoate) yielded only the glycerol  $\alpha$ -methyl ether.

In the latter case, while the  $\alpha$ -ether was the main product, there was also a small amount of the  $\beta$ -derivative present. This was due to its imperfect removal in the purification of the benzoate, since it is admittedly impossible to separate completely all of the solid from the liquid benzoate, but this fact does not affect the conclusions drawn as to the structure of the products.

It is considered proved, therefore, that in the preparation of ethylidene glycerol, a partition occurs between the five and six membered rings, and also that the low boiling acetal has definitely the 1,3-configuration (B) while the higher boiling isomer has the alternate 1,2-structure (A).

**Comparative Properties of the Isomers.**—Four pairs of isomeric glycerol derivatives, namely, 1,2- and 1,3-ethylidene glycerols, their corresponding benzoates, their methyl ethers and  $\alpha$ - and  $\beta$ -glycerol methyl ethers, have now been synthesized and it is believed that their properties offer an interesting physico-chemical study. For purposes of comparison some properties and physical constants are collected in the following table.

Certain generalizations may be drawn from the results in Table I. In all

TABLE I  
PHYSICAL CONSTANTS OF COMPOUNDS

Compound	B. p., °C.	$d_{40}^{17}$	$n_D^{17}$
1,3-Ethylidene glycerol.....	52 (1 mm.)	1.1477	1.4532
1,2-Ethylidene glycerol.....	68-70 (1 mm.)	1.1243	1.4413
1,3-Ethylidene glycerol benzoate.....	(86°)	.....	.....
1,2-Ethylidene glycerol benzoate.....	144-145 (2 mm.)	1.1618	1.5145
1,3-Ethylidene glycerol methyl ether.....	80 (23 mm.)	1.0705	1.4375
1,2-Ethylidene glycerol methyl ether.....	56-58 (23 mm.)	1.0224	1.4177
Glycerol $\beta$ -methyl ether.....	125 (14 mm.)	1.1300	1.4500
Glycerol $\alpha$ -methyl ether.....	111 (13 mm.)	1.1191	1.4460
Glycerol $\beta$ -methyl ether from 1,3-(benzyl- idene glycerol).....	123 (13 mm.)	1.1305	1.4505
Glycerol $\alpha$ -methyl ether from 1,2-(benzyl- idene glycerol).....	110-111 (13 mm.)	1.1197	1.4462

<sup>a</sup> Melting point, crystalline compound.

cases the more symmetrical 1,3-derivatives have higher densities, higher refractive indices and show greater tendency to crystallize (also noted in the benzylidene series) than their isomeric 1,2-forms.

There is one anomaly, however, for which no explanation can be offered. It is seen that the boiling point of the 1,3-ethylidene glycerol is considerably lower than that of the 1,2-derivative, but that when these products are methylated the relative boiling points are reversed, the six membered cyclic form having the higher boiling point. In this connection it should be noted that ethylidene 1,3-propylene glycol, b. p. 108°, and ethylidene 1,2-propylene glycol, b. p. 92°, agree with the relationship of the methylated ethylidene glycerols rather than with the acetals themselves. The various isomers exhibit almost identical properties.

An attempt was made to prepare glycerol  $\alpha$ - and  $\beta$ -monobenzoates starting from the purified isomeric benzoates of ethylidene glycerol and hydrolyzing off the acetal groups with dilute acid but only negative results were obtained.

### Experimental Part

**Preparation of Ethylidene Glycerol from Acetylene.**—The directions given by Hill and Hibbert<sup>9</sup> for the preparation of cyclic acetals from acetylene were followed. Eight g. of mercuric sulfate was triturated in a mortar with 8 cc. of concentrated sulfuric acid, and the resulting paste added, with stirring, to 184 g. (2 moles) of pure glycerol in the reaction flask. After sweeping out the air with acetylene, 45 liters (2 moles) of the latter gas was led in under slight hydrostatic pressure from a gasometer. The reaction flask was surrounded by a water-bath maintained at 70°. After the required amount of acetylene had been absorbed (during about two hours) the reaction product was taken up in ether, filtered and neutralized with solid potassium carbonate. The ether was removed and the product fractionated under reduced pressure. Two hundred and thirty-four g. of mixed ethylidene glycerols was obtained, b. p. 86-101° (20 mm.).

**Preparation of Ethylidene Glycerol from Paraldehyde.**—Two hundred and seventy-six g. of glycerol was mixed with 5 cc. of 50% sulfuric acid in a three-necked flask fitted

with a reflux condenser and a stirrer with a mercury seal. While heating to 100° in a water-bath, 144 g. of paraldehyde was gradually added during the course of one-half hour and the mixture heated for three hours. After cooling, ether was added, the small glycerol layer separated and the ether solution dried over potassium carbonate. Fractionation under reduced pressure yielded 233 g. of mixed ethylidene glycerols, b. p. 79–89 (13 mm.).

**Fractional Distillation of Ethylidene Glycerol.**—Using a long bead fractionating column and diminished pressure, it was possible, by repeated fractionations, to effect a partial separation of the isomeric acetals. From the mixture obtained by the paraldehyde method the sharpest high boiling fraction was obtained, b. p. 80–81° (8 mm.); 187–188 (760 mm.). The mixture from the acetylene method, on the other hand, gave the sharpest low boiling fraction, b. p. 86–88 (20 mm.); 176–177 (760 mm.).

Although these fractions still do not represent completely separated isomers, it was from them that the first definite indication of isomerism was obtained. From them also the benzoates of the isomers were first obtained (using benzoyl chloride with dry pyridine), the low boiling ethylidene glycerol yielding a crystalline product, m. p. 86°, and the high boiling acetal an oil, b. p. 163° (11 mm.). After the properties of these benzoates had been studied the separation of the isomers became a relatively simple matter.

### Determination of Relative Amounts of 1,2- and 1,3-Ethylidene Glycerol Formed by Paraldehyde and Acetylene Methods

The method of isolating and determining the relative amounts of the 1,2- and 1,3-ethylidene glycerols formed depends on the difference in physical character of their benzoates, particularly the difference in solubility in cold ligroin.

Forty-five g. of benzoyl chloride was mixed with 90 cc. of pure, anhydrous pyridine (which had been carefully dried by boiling over barium oxide for 24 hours) and 39 g. of mixed ethylidene glycerols (prepared by the acetylene method, b. p. 94–100° (24 mm.)) added. The reaction was accompanied by the evolution of a large amount of heat. The mixture was allowed to stand for 20 minutes and then added slowly, with constant stirring, to a liter of cold water. The precipitated oil was dissolved in ether, the ether solution washed with 5% sodium hydroxide, then with 3% sulfuric acid, finally with water and dried with potassium carbonate. The ether was removed and the remaining oil heated for two hours at 100° under vacuum to remove traces of pyridine. To this mixture of benzoates was added 100 cc. of ligroin, b. p. 60–70°, and the solution cooled to 0°. Crystals separated out which were washed with cold ligroin and weighed. The remaining oil was fractionated under reduced pressure, yielding the  $\alpha$ -benzoyl derivative. In this way 17 g. of crystalline benzoate (from 1,3-ethylidene glycerol) and 30 g. of liquid benzoate (from 1,2-ethylidene glycerol) were obtained, representing a combined yield of 47 g. or 70%.

The crystalline benzoate melted at 86°. The liquid product boiled at 163° (11 mm.);  $n_D$ , 1.5146;  $d_4^{20}$ , 1.1618. The relative amounts of the low boiling isomer (1,3-ethylidene glycerol) and the high boiling isomer (1,2-ethylidene glycerol) are thus in the ratio of 1 to 1.8.

In the same manner 39 g. of the mixed ethylidene glycerols, prepared by the paraldehyde method, gave a yield of 49 g. (71%) of the mixed benzoates, of which 10 g. was ethylidene glycerol  $\beta$ -benzoate (m. p. 86°) and 39 g. ethylidene glycerol  $\alpha$ -benzoate (b. p. 164° (12.5 mm.);  $n_D$ , 1.5145). The amounts of 1,3-ethylidene glycerol and 1,2-ethylidene glycerol in this case are in the ratio of 1 to 4.

A carefully refractionated sample of ethylidene glycerol, obtained from the low boiling fraction of the acetylene method, and a similarly purified fraction from the high

boiling fraction of the paraldehyde method were benzoylated in a similar manner. In the first case the product was almost exclusively the crystalline benzoate, m. p.  $86^{\circ}$ .

*Anal.* Subs., 0.2200:  $\text{CO}_2$ , 0.5230;  $\text{H}_2\text{O}$ , 0.1245. Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}_4$ : C, 64.86; H, 6.31. Found: 64.83; 6.33.

In the second case the product obtained was an oil, b. p.,  $164^{\circ}$  (12.5 mm.);  $n_D^{20}$ , 1.5146;  $d_4^{20}$ , 1.1618.

*Anal.* Subs., 0.1936:  $\text{CO}_2$ , 0.4603;  $\text{H}_2\text{O}$ , 0.1090. Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}_4$ : C, 64.86; H, 6.31. Found: 64.84; 6.30.

**Preparation of Pure 1,3-Ethylidene Glycerol by Hydrolysis of 1,3-Ethylidene Benzoate.**—Fifty-four g. of 1,3-ethylidene benzoate, m. p.  $86^{\circ}$ , was treated with 15 g. of sodium hydroxide in 150 cc. of water by shaking vigorously and warming until it had melted and completely dissolved. The clear solution was cooled at once and, after adding 100 g. of potassium carbonate, extracted with ether during four hours by means of a continuous extraction apparatus. The ether solution, dried over potassium carbonate and fractionated yielded, besides the solvent, only one product, namely, 17 g. of 1,3-ethylidene glycerol, b. p.  $52^{\circ}$  (2 mm.);  $n_D^{17}$  = 1.4532;  $d_4^{17}$  = 1.1477; yield, 59% of the theoretical. The product was a colorless, nearly odorless oil completely miscible in water.

*Anal.* Subs., 0.1859, 0.1837:  $\text{CO}_2$ , 0.3482, 0.3283;  $\text{H}_2\text{O}$ , 0.1431, 0.1441. Calcd. for  $\text{C}_5\text{H}_{10}\text{O}_3$ : C, 50.84; H, 8.47. Found: C, 50.35, 50.23; H, 8.62, 8.79.

**Preparation of 1,2-Ethylidene Glycerol.**—The liquid 1,2-ethylidene glycerol benzoate used for this preparation was freed as far as possible from the crystalline isomer, as described above, and further by standing at  $-10^{\circ}$  for several days after seeding with the crystalline benzoate. Filtration at  $-10^{\circ}$ , followed by fractionation, gave a nearly pure 1,2-derivative, b. p.  $144\text{--}145^{\circ}$  (2 mm.);  $n_D^{17}$  = 1.5145;  $d_4^{17}$  = 1.1618.

The product was hydrolyzed exactly as in the case of the 1,3-isomer, 140 g. of the benzoate yielding 50 g. of 1,2-ethylidene glycerol, b. p.  $68\text{--}70^{\circ}$  (1 mm.);  $n_D^{17}$  = 1.4415;  $d_4^{17}$  = 1.1243.

*Anal.* Subs., 0.2144, 0.1927:  $\text{CO}_2$ , 0.3965, 0.3555;  $\text{H}_2\text{O}$ , 0.1621, 0.1464. Calcd. for  $\text{C}_5\text{H}_{10}\text{O}_3$ : C, 50.88; H, 8.47. Found: C, 50.39, 50.32; H, 8.47, 8.51.

**Methylation of the Ethylidene Glycerols.**—After using methyl sulfate with poor results, this reaction was carried out successfully with methyl iodide and silver oxide. It was found that efficient agitation greatly increased the yield. Fifteen g. of 1,3-ethylidene glycerol, methylated with 105 g. of methyl iodide and 52 g. of silver oxide gave 15 g. (89% of theoretical) of the corresponding ethylidene glycerol methyl ether, b. p.  $80^{\circ}$  (23 mm.);  $n_D^{17}$  = 1.4375;  $d_4^{17}$  = 1.0705. The product was a colorless oil completely miscible with water.

In the same way 17 g. of 1,2-ethylidene glycerol treated with 110 g. of methyl iodide and 54 g. of silver oxide yielded 16 g. (85% of theory) of a methylated product, b. p.  $53\text{--}58^{\circ}$  (22 mm.). Refractionation gave 14 g., b. p.  $56\text{--}58^{\circ}$  (23 mm.), and a small higher fraction, b. p.  $58\text{--}61^{\circ}$  (23 mm.), which presumably contains some of the 1,3-derivative. The product was a colorless oil, not completely miscible with water, in contrast with its isomer;  $n_D^{17}$  = 1.4177;  $d_4^{17}$  = 1.0224.

**Hydrolysis of Ethylidene Glycerol Methyl Ethers.**—The method used by Irvine and co-workers for the hydrolysis of isopropylidene glycerol methyl ether<sup>8</sup> was followed except that a smaller volume of aqueous alcohol was used. Fifteen grams of 1,3-ethylidene glycerol methyl ether was refluxed for ninety minutes with 50 cc. of 75% aqueous alcohol containing 0.3 cc. of concd. hydrochloric acid. (The theoretical amount of acetaldehyde was collected in a strongly cooled trap, keeping the reflux condenser at  $40\text{--}50^{\circ}$ .) After neutralizing with lead carbonate, filtering, washing the precipitate with

absolute alcohol (adding in all 50 cc. of the latter) and fractionating, 9 g. (72% of theoretical) of pure glycerol  $\beta$ -methyl ether, b. p. 125 (14 mm.), was obtained;  $d_4^{17^\circ} = 1.1300$ ;  $n_D^{17^\circ} = 1.4500$ .

In like manner, 17 g. of 1,2-ethylidene glycerol methyl ether yielded 10 g. of glycerol  $\alpha$ -methyl ether, b. p. 111–112° (13 mm.), and a small higher fraction containing some  $\beta$ -isomer. That the main fraction was a practically pure  $\alpha$ -ether was shown by its refractive index and density,  $n_D^{17^\circ} = 1.4462$  and  $d_4^{17^\circ} = 1.1191$ , compared with  $n_D^{17^\circ} = 1.4460$  and  $d_4^{17^\circ} = 1.1197$  reported by Irvine for pure glycerol methyl ether.

**Hydrolysis of the Isomeric Ethylidene Glycerols.**—Twenty g. of each of the acetals was heated at 130° for one hour with 10 cc. of 5% phosphoric acid, using a reflux condenser maintained at 40°. The latter in turn was connected to a well cooled spiral condenser to collect the acetaldehyde. 20.26 g. of 1,2-ethylidene glycerol (A) gave 7.53 g. of acetaldehyde; yield, 99%. 18.81 g. of 1,3-ethylidene glycerol (B), treated in like manner, gave 6.93 g. of acetaldehyde; yield, 98%.

### Summary

1. The preparation, isolation and quantitative separation of the two isomeric ethylidene glycerols are described.
2. The corresponding methyl ethers and benzoates have been prepared and their physical constants determined.

MONTREAL, CANADA

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

## THE SYNTHESIS OF CERTAIN IODO-ALKOXY ACIDS AND THE MECHANISM OF THE REACTIONS BY WHICH THEY ARE FORMED

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The ready substitution of the chlorine atom in  $\alpha$ -iodo- $\beta$ -chlorophenylpropionic acid by the hydroxyl, methoxyl and ethoxyl groups was demonstrated by Erlenmeyer<sup>1</sup> in 1896. The reaction of  $\alpha$ -iodo- $\beta$ -chlorophenylpropionic acid with water was shown to produce  $\alpha$ -iodo- $\beta$ -hydroxyphenylpropionic acid, while its reaction with solutions of potassium hydroxide in absolute methyl and ethyl alcohols gave, respectively,  $\alpha$ -iodo- $\beta$ -methoxyphenylpropionic acid and  $\alpha$ -iodo- $\beta$ -ethoxyphenylpropionic acid.

In applying the procedure of Erlenmeyer to the synthesis of a variety of  $\alpha$ -iodo- $\beta$ -alkoxyphenylpropionic acids, the fact soon came to our attention that the use of potassium hydroxide is unnecessary. When solutions of  $\alpha$ -iodo- $\beta$ -chlorophenylpropionic acid in a number of different alcohols were allowed to stand for several hours, the  $\alpha$ -iodo- $\beta$ -alkoxyphenylpropionic acids resulted. The yields of the iodo-alkoxy acids depend upon the alcohol, being lowest in the case of *isopropyl* and *tert.*-butyl alcohols. The reaction is not precluded by the substitution of the

<sup>1</sup> Erlenmeyer, *Ann.*, **289**, 259 (1896).