

PREPARATION AND PROPERTIES OF DERIVATIVES
OF 2-(2-ETHOXYETHOXY)ETHANOL

THESIS

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CHAPTER I

INTRODUCTION

In most organic compounds an increase in molecular weight results in a decrease in the solubility in water. This solubility increases with an increase in temperature; however, there are exceptions to this generalization, in that some high-molecular-weight compounds such as polyethylene oxides, $\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{OH}$, in which n may be 100 or more, are readily soluble in water. This phenomenon has been known and reported in the literature for some time. The behavior has been ascribed to the formation of coordination complexes, with water through hydrogen bonding with oxygen atoms, which dissolve in water. Should these coordination bondings be thermolabile, as is the case in most of the 2-(2-ethoxyethoxy)ethanol derivatives investigated in this and other research projects of the department, then the curious solubility behavior of dissolving in cold water and separating out at higher temperatures will be observed.¹

¹ Samuel M. McElvain, The Characterization of Organic Compounds, Revised Edition, pp. 52-53.

A. Why the Problem Was Chosen

Studies in the preparation and properties of 2-(2-ethoxyethoxy)ethanol derivatives carried out previously by Jessie Dorrington,² John L. Bear,³ Charles M. Gliddon,⁴ and Aspet Merijanian⁵ of this chemistry department have involved esters where the 2-(2-ethoxyethoxy)ethyl radical is the alcohol portion of the ester. Thus, for comparative reasons, the present study includes the solubility characteristics of esters where the 2-(2-ethoxyethoxy)ethyl radical is a moiety of the acid portion. Thus, it was decided to synthesize ethyl 2-(2-ethoxyethoxy)ethylmalonate and study its solubility behavior in water at various temperatures to determine whether or not it will exhibit the curious

²Jessie Dorrington, "Some of the Physical Properties of Diethylene Glycol Monoethyl Ether Acetate," Master's Thesis, Southwest Texas State Teachers College, San Marcos, Texas, 1950, p.2.

³John L. Bear, "Preparation and Properties of Derivatives of 2-(2-Ethoxyethoxy)ethanol," Master's Thesis, Southwest Texas State Teachers College, San Marcos, Texas, 1955, pp. 13-27.

⁴Charles M. Gliddon, "Synthesis and Properties of a Homologous Series of Esters of 2-(2-Ethoxyethoxy)ethanol", Master's Thesis, Southwest Texas State Teachers College, San Marcos, Texas, 1958, pp. 5-23.

⁵Aspet Merijanian, "Synthesis and Properties of Diesters of 2-(2-Ethoxyethoxy)ethanol", Master's Thesis, Southwest Texas State Teachers College, San Marcos, Texas, 1958, p. 17.

solubility property at lower temperatures.

Since no account of any amino acid containing the 2-(2-ethoxyethoxy)ethyl radical was noted in the Chemical Abstract indices, it was decided to synthesize 2-amino-4-(2-ethoxyethoxy)butyric acid from ethyl 2-(2-ethoxyethoxy)malonate as an intermediate. Since all known amino acids are solids, the synthesis of this amino acid, 2-amino-4-(2-ethoxyethoxy)butyric acid, was undertaken to determine whether or not definite trends in solubility of a solid derivative of 2-(2-ethoxyethoxy)ethanol could be established.

This paper, in addition, describes the preparation and solubility behavior of ethyl 2-(2-ethoxyethoxy)ethoxyacetate in water. This ester is presented as an example of a monoester whose structure, nevertheless, is rather similar to that of the diester, ethyl 2-(2-ethoxyethoxy)ethylmalonate.

Work on the preparation of 2-(2-ethoxyethoxy)acetaldehyde by direct oxidation of 2-(2-ethoxyethoxy)ethanol is also included in this paper.

B. History and Related Work

Jessie Dorrington,⁶ a student at Southwest Texas State Teachers College, found that 2-(2-ethoxyethoxy)-

⁶Dorrington, op. cit., p. 2.

ethyl acetate has an unusual property of being less soluble in water at high temperatures than at lower temperatures. By this, he demonstrated that 2-(2-ethoxyethoxy)ethyl acetate forms coordination complexes with water, which are thermolabile.

John L. Bear,⁷ a student at Southwest Texas State Teachers College, found that 2-(2-ethoxyethoxy)-ethyl adipate and 2-(2-ethoxyethoxy)ethyl succinate are also more soluble in water at low temperatures than at high temperatures. He demonstrated that the succinate is soluble in all proportions at temperatures less than 25°C., while the adipate is much less soluble. He also synthesized 2-(2-ethoxyethoxy)ethyl benzoate and found its solubility to be too slight to justify further study. Bear attributed the solubility-enhancing property of the 2-(2-ethoxyethoxy)ethyl radical to the hydrogen bonding of the water molecules to the oxygen in the ether linkages, and the dissolving of the resulting hydrates in water. The hydrogen bonds are broken as the temperature of the solution is raised, thus causing the ester to become less soluble.

⁷ Bear, op. cit., pp. 13-27.

Charles M. Gliddon,⁸ also a student at Southwest Texas State Teachers College, prepared and studied 2-(2-ethoxyethoxy)ethyl propionate, 2-(2-ethoxyethoxy)-ethyl butyrate, and 2-(2-ethoxyethoxy)ethyl valerate. The above esters exhibited increased solubility at lower temperatures as well as decreased solubility due to increase in molecular weight. Gliddon pointed out that the propionate was more soluble than the butyrate at low temperatures, where the valerate was completely immiscible at all temperatures.

Aspet Merijanlian,⁹ also a student at Southwest Texas State Teachers College, prepared some diesters of 2-(2-ethoxyethoxy)ethanol and found that unsaturation, as well as substitution of sulfur in place of an oxygen atom, decreased the solubility of these diesters in water.

Riley F. Mogford,¹⁰ a student at Southwest Texas State Teachers College, synthesized derivatives of 2-(2-ethoxyethoxy)ethanol and diethylene glycol and found that 2-(2-ethoxyethoxy)ethyl methallyl ether

⁸Gliddon, op. cit., pp. 5-23.

⁹Merijanlian, op. cit., p. 17.

¹⁰Riley F. Mogford, "Synthesis and Properties of Ether Derivatives of 2-(2-Ethoxyethoxy)ethanol and Diethylene Glycol," Master's Thesis, Southwest Texas State Teachers College, San Marcos, Texas, 1958, pp. 30-31.

and benzyl 2-(2-ethoxyethoxy)ethyl ether were too insignificantly soluble in water to deserve detailed study. However, benzyl 2-(2-ethoxyethoxy)ethyl ether was found to be soluble in concentrated hydrochloric acid in all proportions below 50°C. and less soluble at higher temperatures. Accurate solubility study in hydrogen chloride at higher temperatures could not be made due to cleavage of ether linkages.

Mogford¹¹ also found that allyl 2-(2-ethoxyethoxy)ethyl ether was partially soluble in water while bis(allyloxyethyl) ether was practically insoluble.

Ethyl 2-(2-ethoxyethoxy)ethylmalonate has been reported by V. Hanousek and V. Prelog,¹² as a by-product of the synthesis of isonipecotic acid, by condensing $(ClCH_2CH_2)_2O$ with $CNa_2(CO_2Et)_2$. This compound was synthesized and reported in this paper as a new compound, since no physical constants were reported.

¹¹ Ibid., pp. 30-31.

¹² Chemical Abstracts, Vol. 26, p. 5302.

CHAPTER II

EXPERIMENTAL

A. Ethyl 2-(2-Ethoxyethoxy)ethylmalonate

The method of preparation of ethyl 2-(2-ethoxyethoxy)ethylmalonate was adapted from E. C. Horning.¹

1. Synthesis

To 350 ml. of freshly dried absolute ethanol in a one-liter three-necked round-bottomed flask equipped with a long reflux condenser and a mercury-sealed stirrer was added 17.5 g. of sodium. After all the sodium had reacted, the flask was fitted with a dropping funnel and a calcium chloride tube on top of the condenser.

The flask was heated to about 100°C. (important), and 122 g. of ethyl malonate was added in a steady stream with continuous stirring. After the addition of the ester, 150 g. of 2-(2-ethoxyethoxy)ethyl bromide was added at such a rate that the heat of the reaction caused refluxing. The mixture was then stirred and refluxed for 48 hours. Then the excess ethanol was removed under vacuum. The residue was shaken with 100

¹E. C. Horning, Editor, Organic Syntheses, Collective Volume III, pp. 495-496.

hydroxide was dissolved in 33 ml. of water. To the hot solution, 51 g. of ethyl 2-(2-ethoxyethoxy)ethylmalonate was added in a steady stream with continuous stirring. At this time, ethanol was removed by vacuum, To make saponification complete, the mixture was stirred and heated for 5 hours; and then the content was transferred into a beaker fitted with a stirrer and the solution was cooled in an ice bath until the temperature reached 15°C. Then 40 g. of concentrated solution of technical grade hydrochloric acid was added at such a rate that the temperature did not exceed 20°C. At this point the salt separated. The solution was determined definitely to be acidic to Congo red and transferred to a separatory funnel.

The 2-(2-ethoxyethoxy)ethylmalonic acid was extracted by three 50-ml. portions of ether. The ether solution was transferred into a three-necked flask fitted with a mercury-sealed stirrer, reflux condenser, and dropping funnel. Five milliliters of bromine was added at one time with continuous stirring until decolorized. Then an additional 25 g. of bromine was added slowly enough to avoid violent reaction.

The ether layer containing the bromo-2-(2-ethoxyethoxy)ethylmalonic acid was separated from the aqueous layer, and the ether was removed by distillation from a steam bath.

The residual liquid was decarboxylated by refluxing for 5 hours in a 500-ml. round-bottomed flask on a mantle heated to 130°C. The new bromo acid was separated from the small amount of water and distilled. The fraction boiling at 190°-195°C. under 7-8 mm. mercury pressure was bromo-2-(2-ethoxyethoxy)ethylmalonic acid.

To this bromo acid 400 ml. of technical ammonium hydroxide, twice in excess, was added; and the flask was stoppered tightly and allowed to stand for a week.

Then the mixture was placed on a steam bath; and, under vacuum, water and ammonia were removed until a decrease of 100 ml. in volume was obtained. Then the mixture was cooled to 10°C.; and the first crop of crystals appeared, which was filtered and washed with 10 ml. of ethanol. The filtrate was repeatedly concentrated under vacuum until no further crystals were obtained. The second and following crops of crystals were first washed with 10 ml. of water and then with 95% ethanol. These crystals were assumed to be 2-amino-4-(2-ethoxyethoxy)butyric acid.

2. Physical Data

Decomposition Point.....215°C.

Benzoyl Derivative m.p.....114-115°C.

Color.....White

Solubility

water.....Very soluble
Ethanol.....Soluble
Ether.....Slightly soluble

Remarks: In order to avoid contamination of the amino acid by ammonium bromide, direct concentration of the solution was avoided. To remove the ammonium bromide present in the solution, the mixture was treated with lead hydroxide, thus forming lead bromide and ammonium hydroxide. The lead bromide was filtered off, and the ammonium hydroxide was evaporated under vacuum as ammonia and water.

If the solution was negative to the ninhydrin test for amino acid, it was repeatedly treated with hydrogen sulfide, in order to remove interfering lead ions, until no precipitate appeared after successive filtration.

Upon a positive ninhydrin test, the solution was concentrated and cooled until crystals appeared. If difficulty was encountered in recrystallization from water and alcohol solution, then alcohol and ether had to be used to aid recrystallization.

C. Ethyl 2-(2-Ethoxyethoxy)ethoxyacetate

The method of preparation of ethyl chloroacetate, which was an intermediate for the synthesis of ethyl

2-(2-ethoxyethoxy)ethoxyacetate, was adopted from S. Toole and Frank Sowa.³

1. Synthesis

a. In a 500-ml. three-necked flask fitted with a thermometer, a mercury-sealed stirrer, and a reflux condenser attached to a drying tube, was placed one mole of chloroacetic acid dissolved in two moles of absolute ethanol. To this solution, approximately 2 g. of hydrochloric acid was added and heated at a constant temperature of $50^{\circ}\text{C}.$ $71^{\circ}\text{C}.$ for 5 hours. The mixture was then distilled, and the ethyl chloroacetate was collected at $144-145^{\circ}\text{C}.$ range.

b. To 50 ml. of 2-(2-ethoxyethoxy)ethanol in a 500-ml. three-necked flask, fitted with a mercury-sealed stirrer and a reflux condenser, was added 4 g. of sodium shavings, over a period of three hours. The mixture was gently heated until all the sodium was dissolved.

c. In a 500-ml. Erlenmeyer flask was placed 50g. of the ethyl chloroacetate prepared in step (a) 2:1 in excess of the alkoxide, to which the sodium alkoxide from step (b) was added, with swirling, and left to stand overnight. This mixture was shaken with water and

³S. Toole, and Frank Sowa, "Synthesis of Analogues of Esters of Chloroacetic Acid," Journal of American Chemical Society, Vol. 59, p. 1971, 1937.

the organic layer separated. The water layer was extracted with benzene. The benzene extract was added to the organic layer and distilled under vacuum. The fraction boiling at 169-171^oC. and 44 mm. mercury was collected as the ester.

2. Physical Data

Saponification Equivalent.....	Experimental, 215 Calculated, 220
Refractive Index.....	n_D^{25} , 1.4376
Color.....	Colorless
Boiling Point.....	169-171 ^o C. at 44 mm. mercury pressure
Odor.....	Very slight odor
Solubility	
Benzene.....	Soluble
Water.....	Slightly soluble
Ether.....	Soluble

D. 2-(2-Ethoxyethoxy)acetaldehyde

1. A 500-ml. distilling flask was connected to a one-yard combustion tube packed with 11-12 inches of gauze in the center of it. The combustion tube was put on a 30^o angle and the wire gauze portion enveloped with electrical heating elements. The other end of the tube was connected to wide-bore glass-packed tubing, which in turn was fitted to a water-cooled condenser followed by an adapter and a filter flask. This

receiving flask was kept submerged in ice. A rubber tube connected to the side arm led the generated hydrogen out of the room.

The copper gauze was heated to 500-600°C., and 250 ml. of 2-(2-ethoxyethoxy)ethanol was gently distilled over it and the vapors condensed. This was then fractionally distilled through a 6-foot fractionating column at a constant 6:1 reflux ratio; and the fraction, boiling at 64°C. and 2 mm. mercury pressure, was collected.

The failure to obtain a pure product was attributed to the azeotroping tendency of the alcohol and the aldehyde.

2. Gas Chromatography Analyses

The gas chromatography analyses were done by the Glidden Co.⁴ The simplified interpretation of their analyses is that the areas under each peak in Figures 1 and 2 measure quantitatively, as well as qualitatively, the compound represented. Figure 1 is made from pure 2-(2-ethoxyethoxy)ethanol and Figure 2 represents the aldehyde and the alcohol mixture. The ratio $100 \times a / a+b = 32$ represents percent aldehyde in the

⁴Organic Chemical Division, Glidden Co., Jacksonville, Florida.

mixture, where (a) represents the area containing aldehyde and (b) represents the area of 2-(2-ethoxyethoxy)ethanol.

GAS CHROMATOGRAPHIC ANALYSIS OF PURE
2-(2-ETHOXYETHOXY)ETHANOL

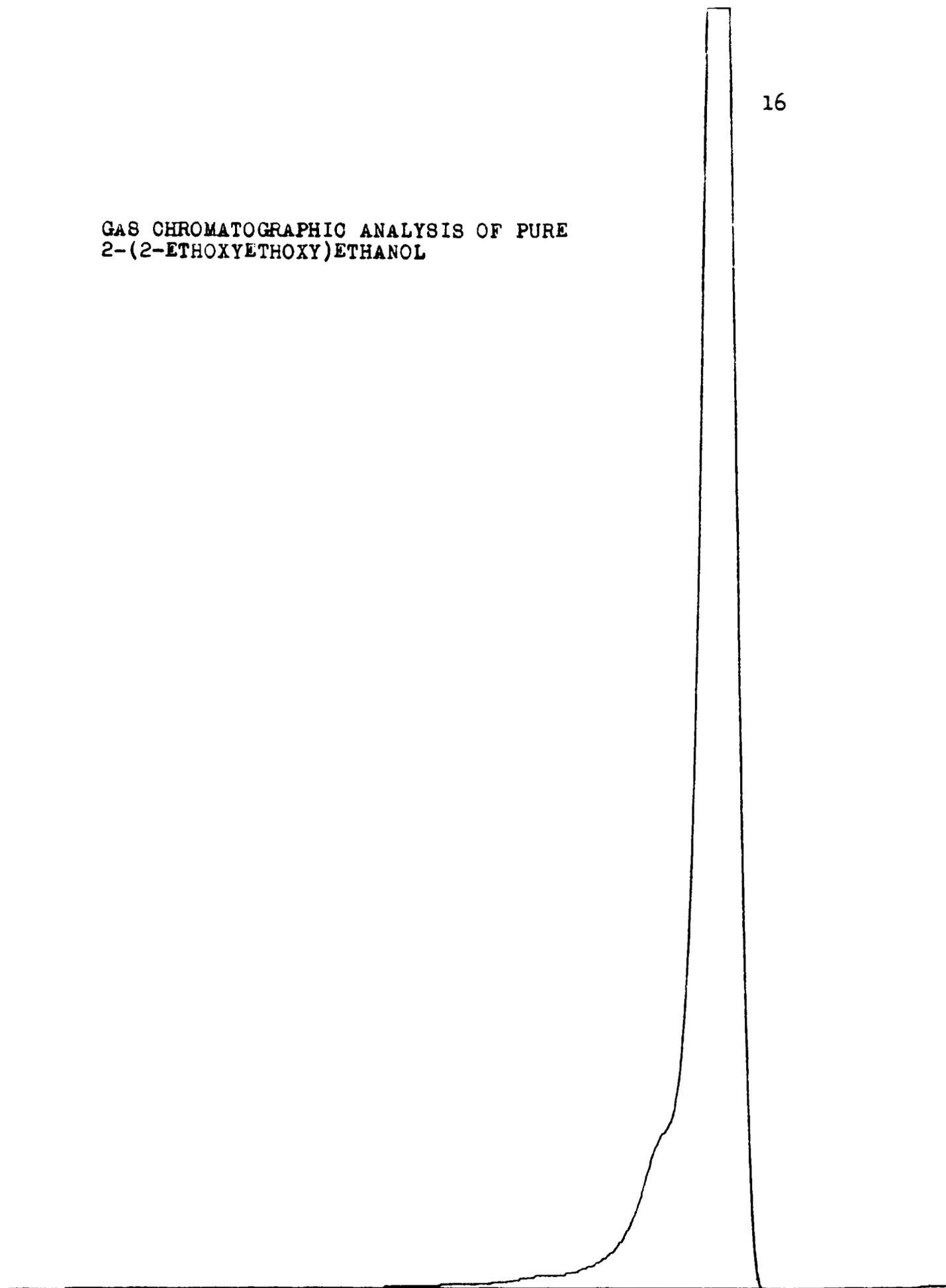


Fig. 1

GAS CHROMATOGRAPHIC ANALYSIS OF
2-(2-ETHOXYETHOXY)ACETALDEHYDE AND
2-(2-ETHOXYETHOXY)ETHANOL MIXTURE

- a. 2-(2-ETHOXYETHOXY)ACETALDEHYDE
b. 2-(2-ETHOXYETHOXY)ETHANOL

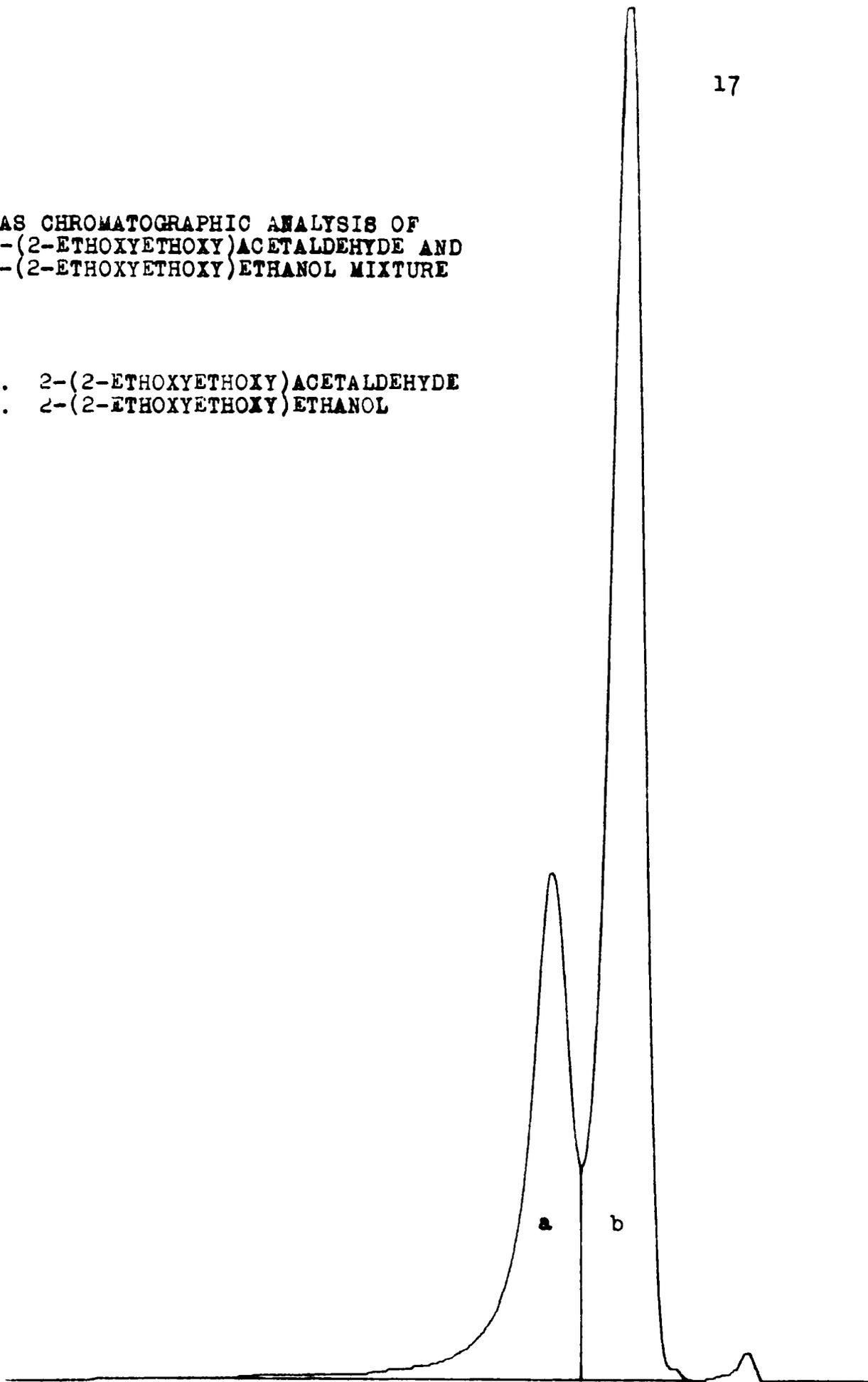


Fig. 2

CHAPTER III

PHASE DIAGRAMS

General Procedure

The data used in the diagrams of these esters were obtained by cooling and heating the different mixtures of ester and water in a 6-inch test tube containing a thermometer and a platinum wire stirrer. This test tube was surrounded by a larger test tube for the purpose of insulation. The temperature was varied until the appearance of the two phases within $\pm 0.5^{\circ}\text{C}$. was reproduced. The approximate temperature range used for the determination of each point was $0-100^{\circ}\text{C}$. at atmospheric pressures.

A. Mutual Solubility of Ethyl 2-(2-Ethoxyethoxy)-ethylmalonate and Water

As it can be noticed in Table I and Graph I, this ester shows a very interesting solubility behavior. At a temperature of 33°C . a mixture of 1.1% ester and 98.9% water is miscible. When the percent of ester is increased to 7.2%, the temperature of miscibility is lowered to 0°C . But as the ester is increased beyond that concentration, it becomes immiscible until the ester concentration exceeds 95%. From this point on complete miscibility was exhibited.

B. Mutual Solubility of Ethyl 2-(2-Ethoxyethoxy)ethoxyacetate and Water

The solubility behavior of ethyl 2-(2-ethoxyethoxy)-ethoxyacetate is similar to that of ethyl 2-(2-ethoxyethoxy)ethylmalonate. However, at 10% ester and 90% water, ethyl 2-(2-ethoxyethoxy)ethoxyacetate is soluble at about 10°C., where, at this concentration of ester and water, ethyl 2-(2-ethoxyethoxy)ethylmalonate is immiscible. It was found that beyond 13.2% ester the mixture is immiscible until the concentration reaches 95% ester and 5% water.

SOLUBILITY OF ETHYL 2-(2-ETHOXYETHOXY)ETHYLMALONATE
IN WATER

No.	Ester (% by weight)	Water (% by weight)	Temperature* °C.
1	1.1	98.9	33
2	2.0	98.0	14
3	3.2	96.8	6.5
4	7.2	92.8	0**
5	95.0	5.0	98***
6	98.0	2.0	98***
7	98.4	1.6	98***

*Temperature above which two phases appear or below which complete miscibility is attained.

**Freezing occurred at this temperature.

***Phase separation was not observed at this temperature.

SOLUBILITY OF ETHYL 2-(2-ETHOXYETHOXY)ETHOXYACETATE
IN WATER

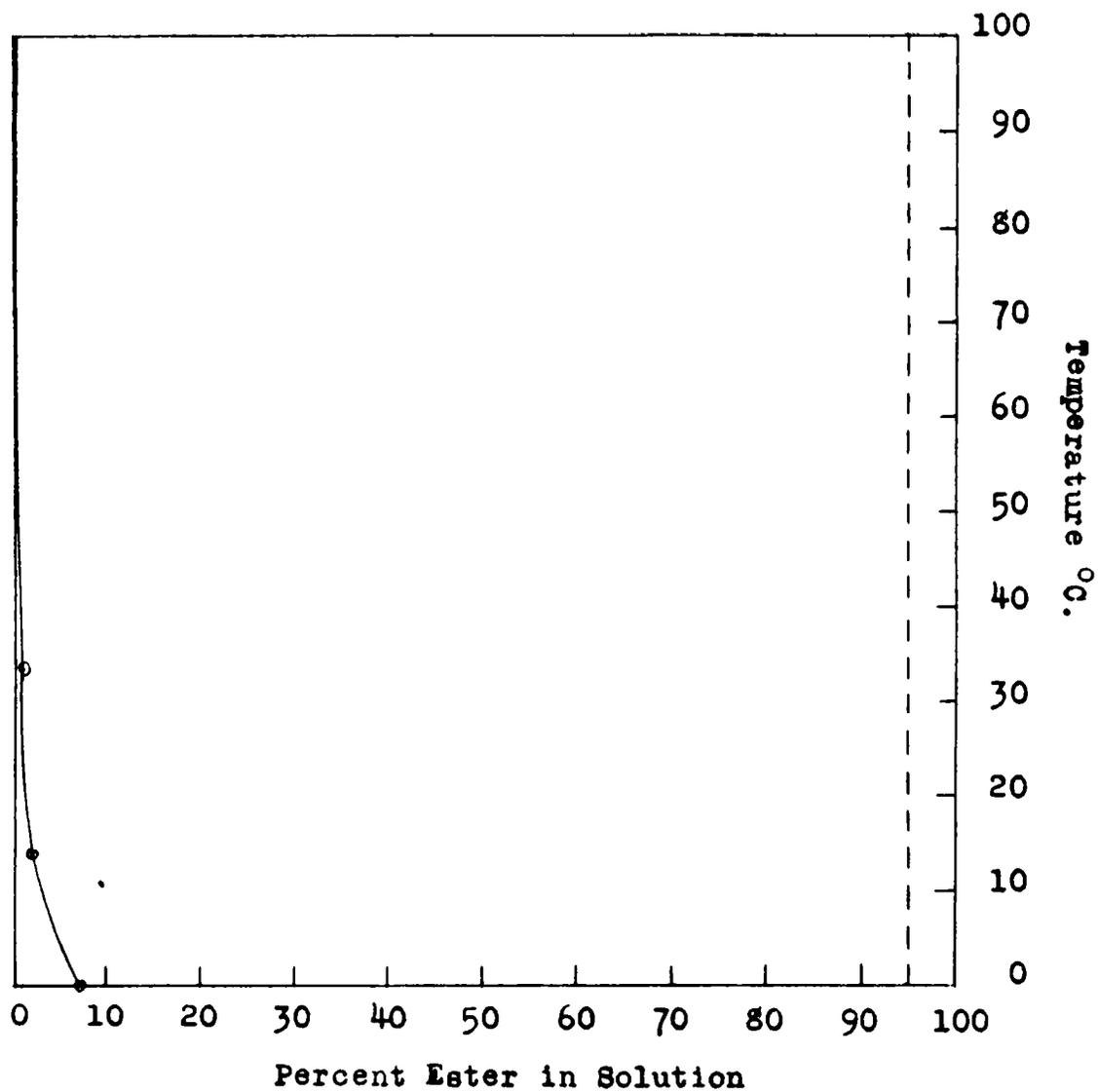
No.	Ester (% by weight)	water (% by weight)	Temperature* °C.
1	7.7	92.3	29
2	10.0	90.0	17
3	13.2	86.8	-3
4	21.5	78.5	-4**
5	95.0	5.0	***
6	95.6	4.4	***
7	97.0	3.0	***

*Temperature above which two phases appear or below which complete miscibility is attained.

**Freezing occurred at this temperature.

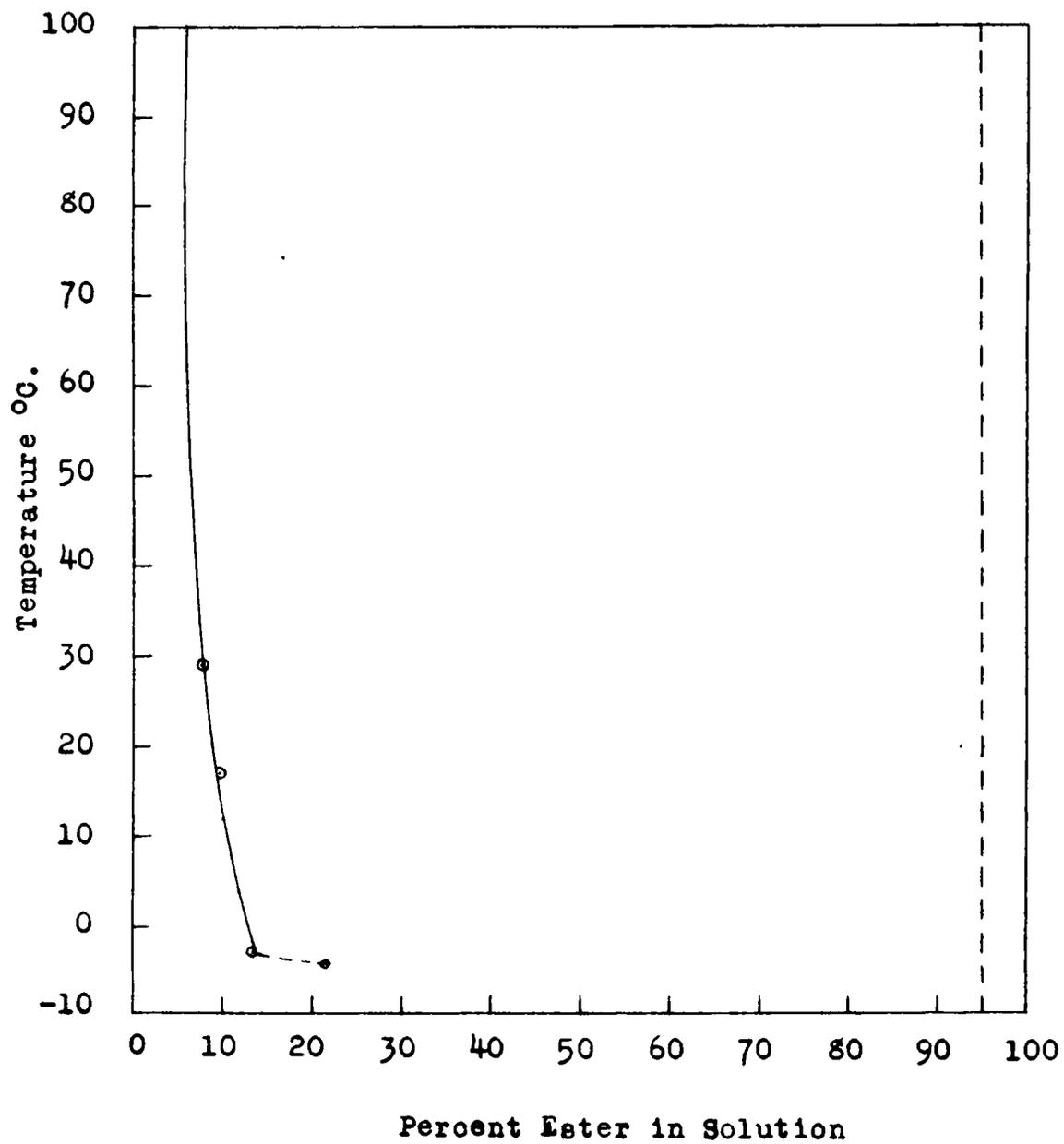
***Phase separation was not observed at this temperature.

MUTUAL SOLUBILITY OF ETHYL 2-(2-ETHOXYETHOXY)ETHYLMALONATE
AND WATER



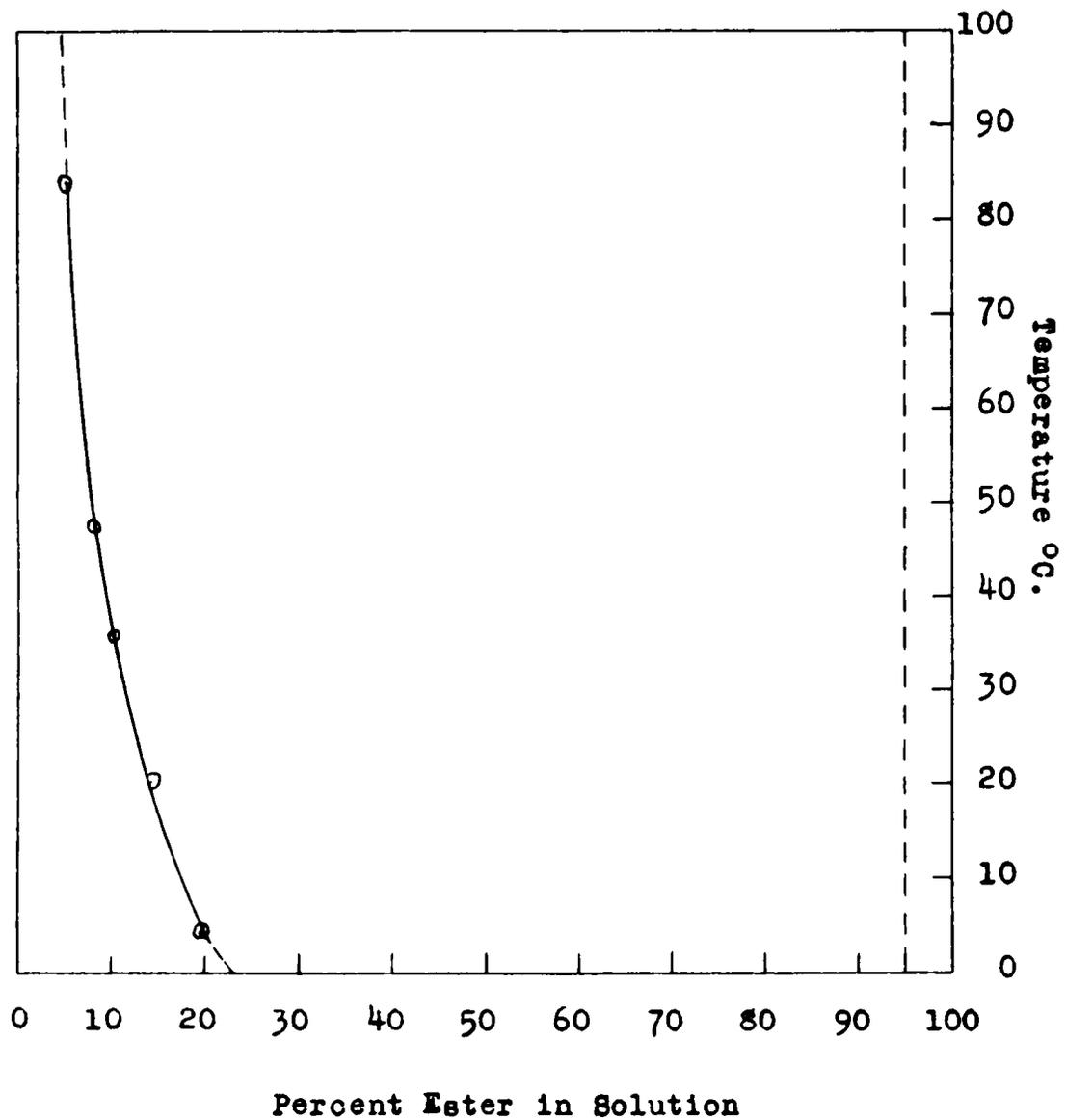
Graph I

MUTUAL SOLUBILITY OF ETHYL 2-(2-ETHOXYETHOXY)ETHOXYACETATE
AND WATER



Graph II

MUTUAL SOLUBILITY OF 2-(2-ETHOXYETHOXY)ETHYL PROPIONATE
AND WATER



Data obtained by Charles M. Gliddon.

Graph III

CHAPTER IV

DISCUSSION

A comparison of solubility behavior of ethyl 2-(2-ethoxyethoxy)ethylmalonate and the ethyl 2-(2-ethoxyethoxy)ethoxyacetate with the other 2-(2-ethoxyethoxy)ethanol derivatives thus far prepared by other students reveals a remarkable similarity in the general shape of the curves. The slope of the curve where the ester is in minority is not as steep as the slope of the curve where the percent of ester is greater than that of water. This is due to the fact that these compounds are more soluble at lower temperatures in the region where the concentration of ester is small. The characteristic solubility curves of these compounds demonstrate the hitherto observed curious behavior of increasing solubility in water at low r rather than higher temperatures in all the 2-(2-ethoxyethoxy)ethanol derivatives. Thus, the deduction that the solubility character of these compounds is mainly due to the polyether chain of the 2-(2-ethoxyethoxy)ethyl radical is rather convincing, if not obvious. A specific illustration of the above conclusion is the great similarity between the solubility behavior of

2-(2-ethoxyethoxy)ethylpropionate¹ and that of the esters presented in this study.

Furthermore, ethyl 2-(2-ethoxyethoxy)ethylmalonate and ethyl 2-(2-ethoxyethoxy)ethoxyacetate are esters of acids which possess the polyether chain. The longer chain exhibits more solubility in water than the shorter, and this can be ascribed to an additional point of hydrogen bonding provided by the extra oxygen atom in the longer chain.

Before the preparation of 2-amino-4-(2-ethoxyethoxy)-butyric acid was undertaken, it was feared that during decarboxylation in strong hydrochloric acid, some of the ether linkage might break. This probably was the case, since a paper chromatographic test indicated the contamination by another amino acid. Due to the great difference in R_f values of the two amino acids, it is evident that one of these is more soluble in water than the other², suggesting a shortened chain, or a loss of an ethoxy linkage. The introduction of the contaminating amino acid, resulting from the rupture of the ether linkages, can be prevented by carefully following the

¹Gliddon, op. cit., pp. 17-18.

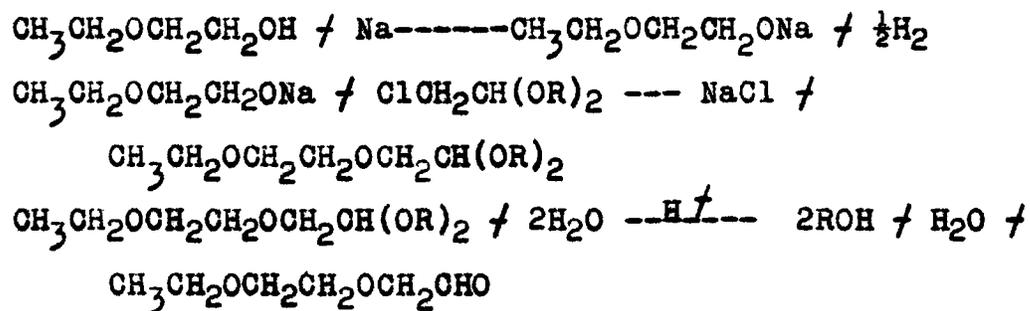
²E. Lederer and M. Lederer, Chromatography, Second Edition, pp. 119-120.

course of acidification of the dibasic salt so that no excess hydrochloric acid is used to encourage the rupture of the ether linkages.

Great difficulty was encountered in recrystallization of this amino acid because of its great solubility in water, making it almost impossible to recrystallize it from water and alcohol mixtures. A few crystals, a relatively small fraction of the total amount dissolved, were obtained from the solution. Nevertheless, the supposedly more water-soluble contaminant persisted as shown by chromatographic analyses. The only method of separation for further purification which the author can suggest is an ion exchange type of separation. Since the facilities for this type of separation were not readily available, the author had to be content with the preparation of a pure derivative of the amino acid. The benzoyl derivative, after 2-7 recrystallizations, melted sharply at 115°C.

The 2-(2-ethoxyethoxy)acetaldehyde was never isolated in pure form; but as is shown in the gas chromatography analyses, the aldehyde was formed and 32% yield was recorded. The phenylhydrazine test on all fractions was positive, confirming a carbonyl group. The melting point of the 2-4-dinitrophenylhydrazine derivative was 115-120°C.

Distillation through a 6-foot column packed with glass helices, at a constant 6:1 reflux ratio under high vacuum, proved to be unsatisfactory. This difficulty could be attributed to the formation of azeotropic mixtures with the alcohol itself. The bisulfite extraction method also proved unsatisfactory. To avoid these difficulties, a different method of synthesis such as outlined below, may well be undertaken:



CHAPTER V

SUMMARY

This paper includes an account of the preparation of four compounds: (a) ethyl 2-(2-ethoxyethoxy)ethylmalonate, (b) 2-amino-4-(2-ethoxyethoxy)butyric acid, (c) ethyl 2-(2-ethoxyethoxy)ethoxyacetate, (d) 2-(2-ethoxyethoxy)acetaldehyde, and the study of their physical properties.

In the case of the malonate and the acetate, phase-diagram studies at various temperatures and concentrations have been made. A comparison of their solubility behaviors with those of esters having 2-(2-ethoxyethoxy)ethyl as the alcohol radical justifies the conclusion that the solubility character of these compounds is mainly due to the polyether chain of the 2-(2-ethoxyethoxy)ethyl radical in the structure of the molecule.

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