THE PREPARATION AND PROPERTIES OF THE CHLOROMETHYL

ETHERS AND FORMALS OF HIGH MOLECULAR WEIGHT ALCOHOLS

A THESIS

Submitted in partial fulfillment
of the requirements for the Degree of
Master of Science in Chemistry

by

Joe Shelby Metcalf

Georgia School of Technology
Atlanta, Georgia
1943

THE PREPARATION AND PROPERTIES OF THE CHLOROMETHYL ETHERS AND FORMALS OF HIGH MOLECULAR WEIGHT ALCOHOLS

Approved:

Date Approved by Chairman May 18, 1943.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. E. Emmett Reid, who suggested the problem, and to Dr. Howard M. Waddle, under whose supervision it was carried out. Their opportune suggestions were of the utmost value.

Thanks are also given to the other members of the faculty who always gave freely of their time and knowledge.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

THE PREPARATION AND PROPERTIES OF THE CHLOROMETHYL ETHERS AND FORMALS OF HIGH MOLECULAR WEIGHT ALCOHOLS

INTRODUCTION

There being few chloromethyl ethers and formals of high molecular weight alcohols known, it was decided to attempt the synthesis of some of these compounds. The alcohols from n-octyl through n-octadecyl were used in these preparations, and, of these, the formal of n-octyl alcohol and the chloromethyl ether of n-octadecyl alcohol have been reported in the literature.

A chloromethyl ether has the general formula CH_2ClOR, a formal $CH_2(OR)_2$, in which the "R" groups may be aryl or alkyl, substituted or unsaturated, or both, and, in the case of the formals, may or may not be alike. In this study, however, "R" represents unsubstituted saturated alkyl groups derived from the corresponding alcohols.

A survey of the available literature revealed the absence of any consistent method of nomenclature of the formals. Quite frequently the naming of a compound appeared to depend upon the author. A complete literature search therefore included looking up the compound under the following headings: common or trade names such as methylal and ethylal for the formals prepared from methyl and ethyl alcohols; acetals; ethers; aldehydes and ketones corresponding to the alkyl groups in question; and the various names given in foreign publications. In this work, to avoid confusion, the method of nomenclature was based on the general type of compound to which the formals belong, and on the materials used in the preparation. For example, the formal prepared from formaldehyde and ethyl alcohol was called formaldehyde-di-ethyl acetal. The derivative from chloromethyl ethyl ether and isopropyl alcohol, having the following structure,

$$CH_2\begin{matrix} \diagup O\text{-}CH_2\text{-}CH_3 \\ \diagdown O\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}CH_3 \end{matrix}$$

would be named formaldehyde-ethyl, isopropyl acetal.

The great reactivity of the chlorine atom in chloromethyl ethers makes them useful for a number of syntheses. For example, they react with cuprous cyanide to give the nitriles, which can be converted into the amides and acids. The acids are alkoxy acetic acids, the higher ones not being well known.

$$ClCH_2\text{-}O\text{-}R + CuCN = CN\text{-}CH_2\text{-}O\text{-}R + CuCl$$

$$CN\text{-}CH_2\text{-}OR + HOH = \begin{matrix} CH_2\text{—}OR \\ | \\ CONH_2 \end{matrix}$$

$$\begin{matrix} CH_2\text{-}OR \\ | \\ CONH_2 \end{matrix} + HOH = \begin{matrix} CH_2\text{—}OR \\ | \\ COOH \end{matrix} + NH_3$$

By reaction with an alcohol the ethers can be converted into formals. This is a convenient method of preparing mixed formals, and the side reactions which would occur by mixing formaldehyde and the different alcohols can thus be avoided. The following equation illustrates such a reaction:

$$ClCH_2\text{-}OR + R'OH = CH_2\begin{matrix} \diagup OR \\ \diagdown OR' \end{matrix} + HCl$$

Chloromethyl-methyl ether in acetic acid condenses without a catalyst on aromatic nuclei.[1] The rate of condensation varies with the functional groups on the aromatic compound. Condensation followed by reduction offers a convenient method of methylating aromatic compounds, as shown by the following reactions:

$$C_6H_6 + ClCH_2O\text{-}CH_3 = C_6H_6(Cl)CH_2\text{-}O\text{-}CH_3$$
$$C_6H_6(Cl)CH_2\text{-}O\text{-}CH_3 + H_2 = C_6H_5CH_3 + HCl + CH_3OH$$

Alpha halogenated ethers, including chloromethyl ethers, react with olefinic hydrocarbons in the presence of readily hydrolyzable metallic halides to give the gamma halo-ethers by addition of the halogen and the ether residue to the unsaturated olefinic linkage.[2] For example, chloromethyl-methyl ether reacts with propylene in the presence of bismuth trichloride to give gamma-chlorobutyl-methyl ether according to the following equation:

$$ClCH_2\text{-}O\text{-}CH_3 + CH_3CH{=}CH_2 = CH_3\text{-}\underset{\displaystyle Cl}{\underset{|}{C}H}\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_3$$

At present formaldehyde-di-methyl acetal (methylal) is the only formal which has been used to any extent in either a practical or theoretical way. However, its various uses seem to indicate that other formals will be of value once they are well known.

---

[1]Vavon, Bolle, and Calin, <u>Bull. soc. chim.</u>, 6: 1025-1033, 1939.

[2]E. I. duPont de Nemours and Company, Brit. 423,520, 1935.

Methylal has been used as a solvent for extractions, and in many cases has been found superior to ether.[3] Acetic, lactic, citric, malic, succinic, and tartaric acids were more completely separated from water by shaking with methylal than by shaking with ether.

Methylal, in which many inorganic salts are soluble, has also been used as a reaction medium,[4] and certain ionic reactions take place in it. For example, mercuric chloride is reduced by stannous chloride in the usual manner.

Grignard reactions may be carried out using methylal as a solvent in place of ether.[5] Care must be taken to use the correct amounts of solvent and reactants to prevent the mixture from becoming partly solid. However, in spite of this added precaution, the method is advantageous because the yields are about ten per cent higher with methylal as the solvent than with ethyl ether.

PURPOSE

The purpose of the problem was to prepare new formals and chloromethyl ethers, to determine the physical properties and percentage yields of the compounds prepared, and to correlate these properties with the structure and size of the molecule.

The investigation was undertaken primarily from an academic viewpoint; no effort was made to find practical uses for the compounds prepared.

---

[3] Espil, Bull. soc. chim., (5) 1:1502-3, 1934.

[4] Bourgom, Bull. soc. chim. Belg., 33:101-15, 1924.

[5] Bourgom, loc. cit.

APPARATUS

Hydrogen Chloride Generator

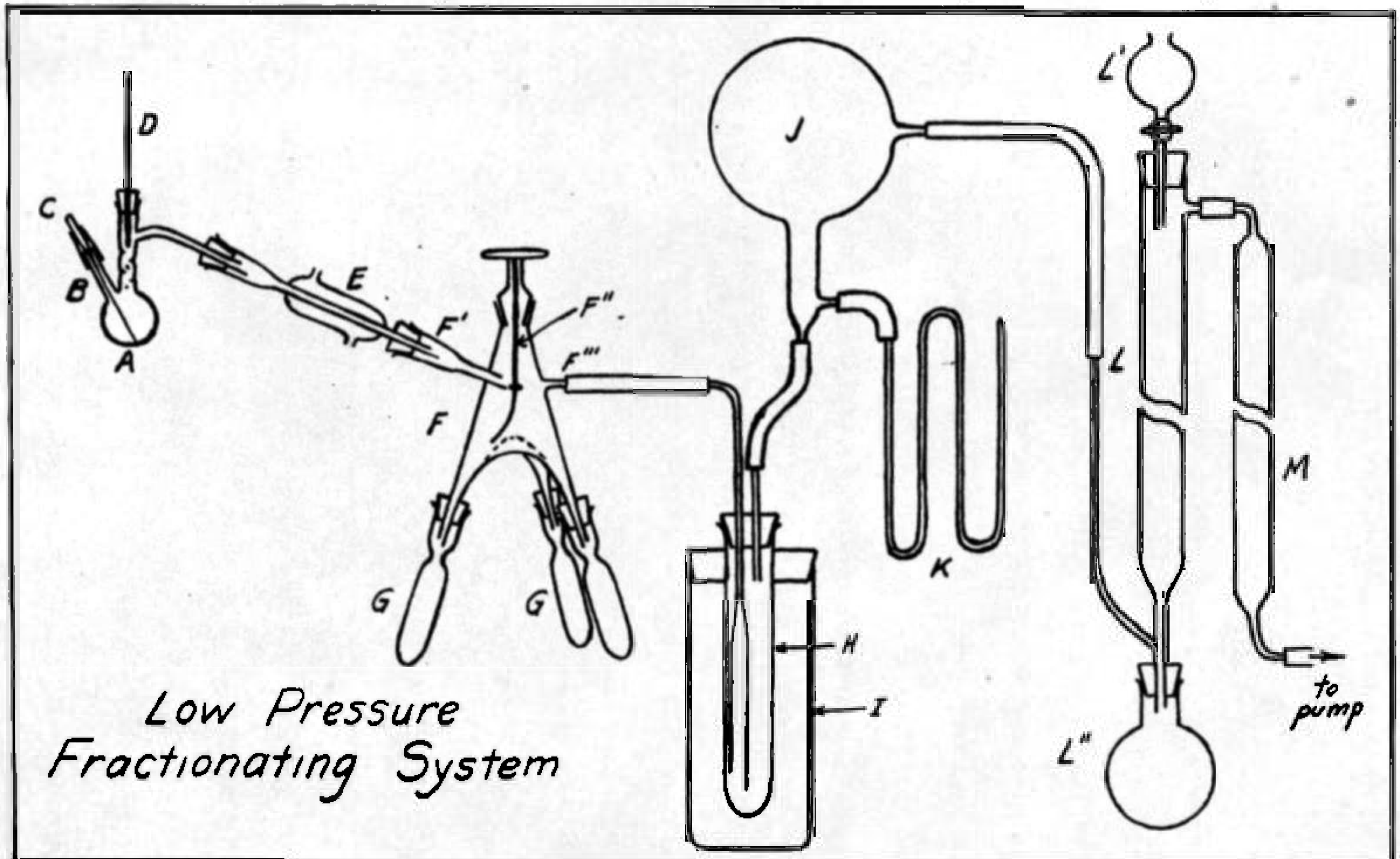
The generator was that described in Inorganic Syntheses.[6]

Reduced Pressure Fractionating System

The preparation of the chloromethyl ethers and formals was carried out on a semimicro scale, using from one to four grams of materials. The fractionating system therefore had to be very small, and the fraction cutter very efficient. The system used is shown in Fig. 1. The material to be fractionated was placed in flask (A), which was made from a 10 cc distilling flask. A side arm (B) was sealed to the side of the flask, and to this was connected an ebullition tube (C), made by drawing a broken thermometer out very fine. This tube was extended to the bottom of the flask, and through it dry air was bubbled very slowly, thus preventing bumping. The neck of flask (A) had several small indentations below the take-off arm, thus making a very short modified Vigreux column. A 360° thermometer was inserted at the top of the flask. The vapors were condensed in a 6-in. all-glass condenser (E), from which the liquid drained into the fraction cutter (F). This piece of equipment was designed by Dr. H. M. Waddle, and proved to be very satisfactory. The side arm (F') extended through the side of the flask, barely touching the glass rod (F''), which was attached to the top of the flask by means of a ground glass joint. Four glass legs were sealed

---

[6] Inorganic Syntheses, (first edition, New York: McGraw-Hill Book Company, Inc., 1939), p 147.



Low Pressure Fractionating System

FIGURE 1

to the bottom of the flask, to which constricted test tubes were attached (G). By turning the rod (F''), the condensed liquid could be directed into any of the four test tubes and sealed off without disturbing the vacuum in any way. From the fraction cutter another side arm (F''') led into a 10-in. test tube (H) immersed in a thermos bottle (I). This bottle was filled with a dry-ice-chloroform mixture, and the extremely low temperature effectively condensed most of the vapors passing through the condenser. The test tube outlet and the mercury manometer (K) were attached to a two-liter flask (J). The purpose of this flask was to minimize pulsations from the vacuum pump, thus assuring a steady pressure throughout the fractionating system. From (J) the vapors were led into the bottom of a sulfuric acid tower (L). Through this concentrated sulfuric acid was slowly dropped from the separatory funnel (L'), the spent acid being collected in flask (L'''). From the top of the sulfuric acid tower the vapors passed into trap (M), which was filled with sodium hydroxide and anhydrous calcium chloride. The bottom of this trap was connected to the vacuum pump.

EXPERIMENTAL PROCEDURE

General Discussion

Many methods are known for the preparation of chloromethyl ethers and formals, the more important being described in Beilstein's Handbuch Der Organischen Chemie.[7] The method suggested by Dr. E. E. Reid[8] and

[7] Beilstein, Handbuch Der Organischen Chemie, Vierte Auflage, Band I, pp 574-582.
Ibid, Erstes Ergänzungswerk, pp 301-305.

[8] Private communication from Dr. E. E. Reid to T. S. Stanislaw.

successfully used by T. S. Stanislaw[9] required no elaborate equipment or unavailable materials, and was therefore selected for this work.

Preparations of chloromethyl ethers were attempted from the following alcohols: n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, and n-octadecyl; formals from n-octyl, n-decyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, and n-octadecyl. It is now known that none of the chloromethyl ethers were prepared, probably because of decomposition during fractionation. All of the formals were prepared, and only one of these, formaldehyde-di-n-octyl acetal, has been reported in the literature.

Preparation of Chloromethyl Ethers

To prepare the chloromethyl ethers, one to four grams of the alcohol were placed in a 6-in. test tube with an equivalent amount of U.S.P. paraformaldehyde, the ratio of alcohol to paraformaldehyde being one mole to one equivalent. Not more than one milligram of C.P. potassium hydroxide was added as catalyst, and the mixture heated in a constant temperature water bath with occasional shaking until homogeneity resulted. The temperatures varied from 60°C for decyl alcohol to 80°C for octadecyl alcohol. This rise in temperature was necessary because of the rather high melting points of the higher alcohols. The time required for homogeneity to result was usually not more than thirty minutes, and frequently only ten minutes. An excess of dry hydrogen chloride was then passed into the mixture. Theoretically, only one mole of hydrogen

[9] Stanislaw, T. S., (Unpublished Thesis), Georgia School of Technology, 1942, pp 18-19.

chloride would have been necessary to yield one mole of ether. The excess gas was necessary to force the reaction more nearly to completion and to cause the separation of the water layer. The formation of the chloromethyl ethers took place according to the following reactions in which "R" is an alkyl group.[10]

$$HCHO + ROH = CH_2OHOR$$
$$CH_2OHOR + HCl = ClCH_2OR + H_2O$$

The water layer was separated from the ether by means of a long, thin medicine dropper, after which the ether was dried over anhydrous calcium chloride. To remove the excess hydrogen chloride, the ether was transferred from the test tube to the flask in the fractionating system. The dry-ice-chloroform trap was put in place, and reduced pressure from an aspirator applied. The flask was heated to 30-40°C in an oil bath, and the excess hydrogen chloride was quickly and efficiently removed. Because of the small amount of gas present, a horizontal sodium hydroxide trap was not necessary. The dry-ice trap effectively condensed any volatile liquids.

The dry chloromethyl ether was then fractionated twice at 2-7 mm pressure as described on p 5. Water had to be carefully excluded at all times, since hydrolysis readily took place, even upon exposure to the atmosphere. The hydrolysis of the chloromethyl ethers in neutral or alkaline medium takes place according to the following equations:

---

[10]Richter, <u>Textbook of Organic Chemistry</u>, (New York: John Wiley and Sons, Inc., 1938), p 166.

$$ClCH_2OR + HOH = HOCH_2OR + HCl$$
$$HOCH_2OR \rightleftharpoons HCHO + ROH$$

The hemiacetal first formed is unstable and immediately decomposes into formaldehyde and the alcohol from which the ether was prepared.[11]

Preparation of Formals

To prepare the formals, one or two grams of the alcohol were mixed with an equivalent amount of U.S.P. paraformaldehyde in a 6-in. test tube, using two moles of the alcohol per equivalent of paraformaldehyde. Approximately 0.5 mg of C.P. potassium hydroxide was added as catalyst, and the mixture made homogeneous at 60-85°C in the same manner as the chloromethyl ethers. Dry hydrogen chloride was then passed into the hot solution until it became cloudy, after which it was immediately neutralized with hot 10 per cent sodium carbonate solution to prevent hydrolysis. The formal was washed free from chlorides with hot distilled water. If liquid, the formal was dried over anhydrous calcium chloride and fractionated; if solid, it was dissolved in approximately three cubic centimeters of benzene and the resulting solution dried over calcium chloride. Most of the benzene was removed by evaporation on a hot plate, and the formal crystallized on cooling. The solid formals were purified by repeated crystallizations from a hot benzene-ethyl alcohol mixture. The formals were dissolved in a small amount of hot benzene, 95 per cent ethyl alcohol was added until the cloudiness disappeared, and the hot solution cooled slowly to room temperature. The white, flaky crystals were then separated by filtration.

---

[11] Ibid, p 103.

The formation of the formals took place as shown by the following equations, in which "R" is an alkyl group.[12]

$$HCHO + HOR = HOCH_2OR$$
$$HOCH_2OR + ROH = CH_2(OR)_2 + HOH$$

According to Skrabal and Schiffrer,[13] alkyl acetals are hydrolyzed only in an acid solution, as illustrated by the following equations:

$$CH_2(OR)_2 + HOH = CH_2(OH)OR + ROH$$
$$CH_2(OH)OR = HCHO + ROH$$

The small amount of water liberated when hydrogen chloride was passed into the homogeneous mixture was not sufficient to form a layer, and great care had to be taken to prevent using excess gas, since this would cause hydrolysis of the formal, as illustrated in the above equations.

Characterization of Chloromethyl Ethers

To determine whether or not the desired ether had been prepared, the percentage of chlorine was determined quantitatively, and, if the compound was a liquid, its molar refraction was calculated. If the found values checked reasonably well with the theoretical values, it could then be assumed that the desired compound had been prepared.

The method of chlorine analysis used was essentially a combination of modified Stepanow and Volhard procedures, as described by Drogin and Rosanoff[14] and Cook and Cook.[15]

---

[12] Ibid.

[13] Skrabal and Schiffrer, Z. physik. chem., 99: 290-313, 1921.

[14] Drogin and Rosanoff, J. Am. Chem. Soc., 38: 711, 1916.

[15] Cook and Cook, Ind. and Eng. Chem., 5: 186-88, 1933.

For the analysis 0.1500-0.4000 g of the refractionated ether was sealed in a small glass ampule made by drawing out glass tubing to the diameter of a large melting-point tube and blowing a bulb on the end which would hold 0.15-0.40 g of the compound. The ampule was dropped into a 500-cc Kjeldahl flask containing 75 cc of absolute alcohol. The impact of the drop was great enough to break the ampule, and a solution of the alcohol and ether resulted. The flask was stoppered immediately, shaken, and allowed to stand for several minutes. A reflux condenser was attached, and through it was added, during a thirty minute interval, 5 g of oxide-free, dry sodium cut into thin strips about one inch long. The mixture was heated gently during the addition of the last half of the sodium and then refluxed from a water bath for one hour. The following reaction took place:

$$ClCH_2OR + C_2H_5ONa = CH_2(OR)OC_2H_5 + NaCl$$

The mixture was cooled, diluted with 200 cc of distilled water, and acidified with nitric acid of specific gravity 1.202, care being taken to add not more than 10 cc in excess. The volume of C.P. 0.1006 N silver nitrate solution calculated to precipitate all of the chloride was added slowly, and then 10 cc in excess. One cubic centimeter of nitrobenzene was added for each 50 mg of chlorine in the original sample to coagulate the precipitated silver halide. The mixture was shaken vigorously until flaky silver chloride separated from the remaining liquid. The mixture was quantitatively transferred from the Kjeldahl flask to a one-liter porcelain evaporating dish, and 10 cc of a saturated solution of ferric-alum-nitric acid indicator was added. The excess silver nitrate was determined by titration with a 0.0512 N solution of C.P. potassium thiocyanate. The nitrobenzene formed a film over the precipitated silver chloride, thus preventing reaction of the halide with potassium thiocyanate and making filtration unnecessary.

A blank determination was run on the reagents for each set of analyses. In the calculations, this blank value was added to the volume of excess silver nitrate as determined from the back titration with potassium thiocyanate, and the resulting sum was subtracted from the volume of the standard silver nitrate originally added. This difference was equivalent to the chlorine in the sample.

The results of these analyses are summarized in Table II.

Characterization of the Formals

The formals were characterized entirely by physical methods. Their identity was shown by determining their molecular weights by the method of freezing-point lowering and, if the compounds were liquids, calculating their molecular refractions. The results of these determinations are summarized in Table I.

The apparatus and method used in the molecular weight determinations are described in Daniels' Experimental Physical Chemistry.[16] The molecular weights were calculated from the following formula:

$$M = k \cdot \frac{w}{dW}$$

where M is the molecular weight sought, w the weight of the solute, d

[16] Daniels, Mathews, and Williams, Experimental Physical Chemistry, second edition, (New York, McGraw-Hill Book Company, Inc., 1934) pp 58-64.

TABLE I

PROPERTIES OF THE PREPARED FORMALS

COMPOUND		Formaldehyde di-n-octyl acetal	Formaldehyde di-n-decyl acetal
FORMULA		$CH_2(O\ C_8H_{17})_2$	$CH_2(O\ C_{10}H_{21})$
DIST.	TEMP. °C	161-171	196-197.5 (M.P. 17°C)
	PRESS. mm	7	5
MOL. WGT.	FOUND	266.9	329.5
	CALCD.	272.46	328.56
d^{25}_{4}		0.8423[a] 0.8591(0°C)	0.8445
n^{25}_{D}		1.4319[b] 1.4412(0.6°C)	1.4388
M_D	FOUND	83.88 83.83(0°C)	102.29
	CALCD.	83.99	104.46
PERCENT YIELD		62.5	29

[a]A previously calibrated pycnometer in a constant temperature bath was used.

[b]An Abbé Refractometer was used with water at the required temperature circulating through it.

TABLE I (Cont.)

PROPERTIES OF THE PREPARED FORMALS

COMPOUND		Formaldehyde di-n-dodecyl acetal	Formaldehyde di-n-tridecyl acetal	Formaldehyde di-n-tetradecyl acetal	Formaldehyde di-n-pentadecyl acetal
FORMULA		$CH_2(O\ C_{12}H_{25})_2$	$CH_2(O\ C_{13}H_{27})_2$	$CH_2(O\ C_{14}H_{29})_2$	$CH_2(O\ C_{15}H_{31})_2$
MELTING POINT °C		29	37-37.5	41.5-42	47.5-48
MOL. WGT.	FOUND	383.8	417.8	438.2	458.1
	CALCD.	384.67	412.72	440.77	468.82
n_D^{60}		1.4309	1.4329	1.4344	1.4369
PERCENT YIELD		48.5	36.3	62	48.3

TABLE I (Cont.)

PROPERTIES OF THE PREPARED FORMALS

COMPOUND		Formaldehyde di-n-hexadecyl acetal	Formaldehyde di-n-heptadecyl acetal	Formaldehyde di-n-octadecyl acetal
FORMULA		$CH_2(O\ C_{16}H_{33})_2$	$CH_2(O\ C_{17}H_{35})_2$	$CH_2(O\ C_{18}H_{37})_2$
MELTING POINT °C		50	54-55	59
MOL. WGT.	FOUND	506.0	512.4	546.6
	CALCD.	496.87	524.93	552.98
n_D^{60}		1.4390	1.4399	1.4406
PERCENT YIELD		50.9[c]	36.3	52.2

[c]The use of small quantities of materials and the loss through repeated crystallizations account for the rather low yields.

the freezing point depression, W the weight of solvent, and k a constant depending only on the solvent. Benzene and cyclohexane were the solvents used, k having the values 5120 and 20,000 respectively.

The observed molecular refractions were calculated from the Lorenz-Lorentz equation,[17]

$$M_D = \frac{n^2 - 1}{n^2 - 2} \cdot \frac{m}{d}$$

in which M_D is the observed molecular refraction, n the refractive index, m the molecular weight of the compound in question calculated from the atomic weights, and d the density determined experimentally.

The calculated molecular refractions were obtained by adding the atomic refractions given in Lange's Handbook of Chemistry.[18]

DISCUSSION OF THE PREPARATION AND PURIFICATION OF CHLOROMETHYL ETHERS

Since the method used for the preparation and purification of chloromethyl ethers had previously been proven satisfactory, the great difficulty encountered in the purification of the ethers was unexpected.

In each of the five preparations attempted, the ethers appeared to be formed as expected. In each case a water layer separated on passing dry hydrogen chloride into the homogeneous reaction mixture, and the large excess of the gas used should have prevented the formation of the corresponding formal.

---

[17] Lange, N.A., Handbook of Chemistry, fourth edition, Sandusky, Ohio: Handbook Publishers, Inc., 1941, p 875.

[18] loc. cit.

However, when low pressure fractionation was attempted, only part of the liquid could be collected, even though the temperature of the oil bath was raised as much as 100°C above the expected boiling point. The liquid tended to reflux in the column, and only occasionally would a drop be forced over. Analysis of the portion collected showed that it contained chlorine, but the percentage was much too low. The residue in the flask contained no chlorine. This would seem to indicate that at the boiling points the ethers partially decomposed, yielding the alcohols originally used. The alcohol would then react with the remaining chloromethyl ether to form the corresponding formal. This was definitely shown in the attempted fractionation of chloromethyl-n-decyl ether. The boiling point should have been approximately 100°C at 2 mm pressure, but only two or three drops came over, even though the bath temperature reached 180°C. However, when the bath temperature reached 220°C all the contents of the flask fractionated smoothly. A check on the physical properties showed the product to be formaldehyde-di-n-decyl acetal. The chloroform-dry-ice trap contained no trace of either a liquid or solid, but some volatile substance reacted with the acid in the sulfuric acid tower. The decomposition of the chloromethyl ethers may have been caused by heat or the presence of small amounts of water or hydrogen chloride. Water would cause the ether to hydrolyze, forming the corresponding alcohol, formaldehyde, and hydrogen chloride. At a high temperature, a trace of hydrogen chloride might break the ether linkage, though such reactions are usually carried out at high rather than low pressures. No positive explanation can be offered for the behavior of the chloromethyl ethers.

TABLE II

PROPERTIES OF THE PREPARED CHLOROMETHYL ETHERS

COMPOUND		Chloromethyl-n-decyl ether	Chloromethyl-n-dodecyl ether	Chloromethyl-n-tetradecyl ether
FORMULA		$CH_2Cl\ O\ C_{10}H_{21}$	$CH_2Cl\ O\ C_{12}H_{25}$	$CH_2Cl\ O\ C_{14}H_{28}$
DIST.	TEMP. °C		140-141	158-160
	PRESS. mm		7	5-6
PER CENT Cl	FOUND		11.22	10.90
	CALCD.		17.15	15.10
d_4^{25}		0.8661	0.8992	0.8938
n_4^{25}		1.4369	1.4488	1.4470
M_D	FOUND	62.6	70.0	78.5
	CALCD.	59.51	68.74	77.98
PERCENT YIELD		1	47	41

TABLE II (Cont.)

PROPERTIES OF THE PREPARED CHLOROMETHYL ETHERS

COMPOUND		Chloromethyl-n-hexadecyl ether	Chloromethyl-n-octadecyl ether
DIST.	TEMP. °C	172-175	179-180.5
	PRESS. mm	4	2
MELTING POINT		26°	40°
PER CENT Cl	FOUND	10.05	9.67
	CALCD.	12.19	11.12
n_D^{51}			1.4428
n_D^{52}		1.4397	
PERCENT YIELD		46	21

SUMMARY

The following heretofore unreported compounds have been prepared and some of their common physical properties determined: formaldehyde-di-n-decyl acetal, formaldehyde-di-n-dodecyl acetal, formaldehyde-di-n-tridecyl acetal, formaldehyde-di-n-tetradecyl acetal, formaldehyde-di-n-pentadecyl acetal, formaldehyde-di-n-hexadecyl acetal, formaldehyde-di-n-heptadecyl acetal, and formaldehyde-di-n-octadecyl acetal. Formaldehyde-di-n-octyl acetal was also prepared, and the physical properties determined checked closely with those listed in the literature. The structures and physical properties of these compounds are summarized in Table I (pp 14-16).

Five chloromethyl ethers were apparently prepared, but evidently decomposed on attempted fractionation, since no satisfactory products could be isolated. The results of the chlorine analyses and physical properties are summarized in Table II (pp 19-20).

BIBLIOGRAPHY

Beilstein, Handbuch Der Organischen Chemie, Vierte Auflage, Band I, Berlin: Julius Springer, 1918, pp 574-582.

______, Handbuch Der Organischen Chemie, Vierte Auflage, Band I, Erstes Erganzungswerk, Berlin, Julius Springer, 1918, pp 301-305.

Bourgom, A., Bulletin de la societe chimique de Belgique, 33: 101-115, 1924.

Cook, W. A. and Cook, K. H., Industrial and Engineering Chemistry, analytical edition, 5: 186-188, 1933.

Daniels, F., Mathews, J.H., and Williams, J.W., Experimental Physical Chemistry, second edition, (New York, McGraw-Hill Book Company, Inc., 1934), pp 58-64.

Drogin, I., and Rosanoff, M.A., Journal of the American Chemical Society, 38: 711, 1916.

E. I. du Pont deNemours and Co., British patent 423,520, 1935.

Espil, L., Bulletin de la societe chemique de France Memoires, (5) 1: 1502-1503, 1934.

Inorganic Syntheses, first edition, New York: McGraw-Hill Book Co., Inc., 1939, p 147.

Lange, N.A., Handbook of Chemistry, fourth edition, Sandusky, Ohio: Handbook Publishers, Inc., 1941 p 875.

Reid, E. E., private communication from E. E. Reid to T. S. Stanislaw.

Richter, G. H., Textbook of Organic Chemistry, New York: John Wiley and Sons, Inc., 1938, p 166.

Skrabal, A., and Schiffrer, A., Zeitschrift fur Physikalische Chemie, 99: 290-313, 1921.

Stanislaw, T. S., (Unpublished Thesis), Georgia School of Technology, 1942.

Vavon, G., Bolle, J., and Calin, J., Bulletin de la societe chemique de France Memoires, 6: 1025-1033, 1939.