CONDENSATION OF SOME OCTYL ALCOHOLS WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE METHYL DI PROPYL CARBINOLS

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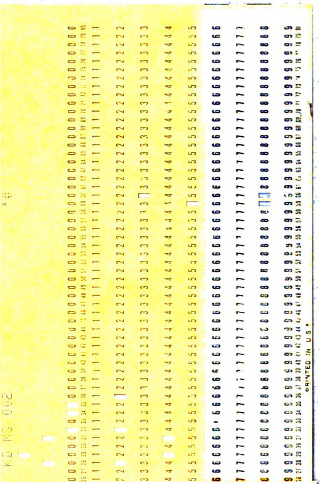

CONDENSATION OF SOME OCTYL ALCOHOLS WITH BENZENE
IN THE PRESENCE OF ALUMINUM CHLORIDE
METHYL DI PROPYL CARBINOLS

by

Kenneth Dale Cline

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Contents

INTRODUCTION

INTRODUCTION

The process of condensation is connected with the early history of organic chemistry and was the outcome of the first systematic attempts at organic chemistry.

Condensation may be defined as "the union of two or more organic molecules or parts of the same molecule (with or without elimination of component elements) in which the new combination is effected between carbon atoms".

There are two types, external condensation in which two or more different molecules become linked together and internal condensation in which carbon atoms in the same molecule combine, leading to ring formation.

It will be observed that union between molecules or parts of a molecule is nearly always determined by unsaturation and by a consequent tendency for the unsaturated atoms to saturate themselves. There are two groups: those in which the combining molecules are induced to unite by being rendered, as it were, artificially unsaturated as the result of withdrawing certain elements and those which, being already unsaturated, combine either spontaneously or with the help of a reagent or catalyst.

Condensation by the separation of the elements may be divided into catalytic and dehydrative reactions. However, these may be united again when the reagent used may serve both purposes in the same reaction. The workers in this laboratory, however, have been especially interested in the condensation reactions in which water is apparently split from the alcohols.

These are three mechanisms for the explanation of the catalytic action of aluminum chloride:

First, proposed that the formation of an unsaturated compound (dehydration of the alcohol) is the essential intermediate in the catalytic action.

Second, states that the formation of an alkyl halide is necessary for aluminum chloride to act as a catalyst.

Third, suggests that the preliminary action of aluminum chloride followed by rearrangement is the true explanation.

The Lewis-Kossel theory (1) offers the best explanation although it is somewhat indefinite. The catalyst unites with the substance catalyzed through some of the electrons of the outer shell of the atoms of the molecule. The new arrangement of atoms and electrons is unstable at the temperature of the reaction. Rearrangement of the atoms and electrons then takes place to form more stable systems.

HISTORY

HISTORY

Many dehydration agents have been employed in the condensation of various compounds to give a new field of organic chemistry. Catalyst which have been used are; sulfuric acid, phosphoric acid, phosphorous pentoxide, magnesium chloride, zinc chloride, phosphorous pentachloride, aluminum chloride, ferric chloride, (both anhydrous and $FeCl_3 \cdot 6H_2O$), stannic chloride, acetic acid, sulfuric and acetic acid mixture, and hydrogen chloride. The condensation catalysts listed below have, however, proven more efficient, so at least one example of each is given.

Zinc chloride was used by Fisher and Roser (2) to prepare aminotriphenylmethane by the condensation of benzhydrol and aniline hydrochloride.

Sulfuric acid was used in 1880 when Becker (3) condensed m-nitrobenzyl alcohol and benzene to give m-nitrodiphenylmethane.

Sulfuric and acetic acid mixtures were used by Meyer and Wurster (4) to condense benzyl alcohol and benzene to give diphenylmethane.

Stannic chloride was used by Micheal and Jeanpretre (5) when they prepared phenyl trimethylphenylacetonitrile by the condensation of mesitylene with phenylhydroxyacetonitrile.

Phosphorous pentoxide was employed by Hamilian (6) to prepare diphenyl p-xylymethane from benxhydrol and p-xylene.

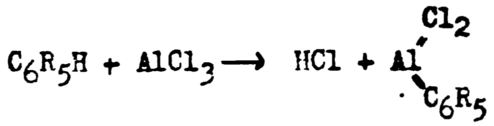
Magnesium chloride was used by Mazzara (7) in the preparation of propyl m-cresol from the condensation of propyl alcohol and m-cresol.

Hydrogen chloride has been used as was shown by Noelting (8) in the preparation of p-nitrodimethyldiaminodiphenyltolylmethane.

Acetic acid was used by Rhotinski and Patzewitch (9) to condense triphenyl carbinols with pyrrole.

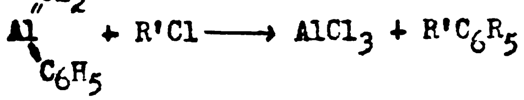
The workers in this laboratory, however, have been especially interested in the use of aluminum chloride and the mechanism by which the reaction takes place. Therefore I will elaborate on this condensing agent to give a more complete picture of its use.

Aluminum chloride was introduced as a catalyst in the condensation reactions by the works of Friedel and Craft (10) in 1877. Their work was held within the bounds of the aliphatic series, however, they stated that it would not hold for the aromatic series. This has been disproven as have many theories by further research. The catalytic activities in Friedel and Crafts reactions of the anhydrous aluminum chloride may be explained by the production of a temporary combination between the chloride and the organic material.



$$C_6R_5H + AlCl_3 \longrightarrow HCl + Al\genfrac{}{}{0pt}{}{Cl_2}{C_6R_5}$$

the latter would react with the halide.



$$Al\genfrac{}{}{0pt}{}{Cl_2}{C_6H_5} + R'Cl \longrightarrow AlCl_3 + R'C_6R_5$$

Merz and Weith (11) condensed phenol with itself to form diphenyl ether by the use of aluminum chloride. Wass (12) by condensing dichloroethyl oxide with benzene obtained triphenylethane. It is shown here that undoubtedly the aluminum chloride serves not only as a catalyst but also as a dehydrating agent. Graebe (13) condensed benzene and hydroxylamine in the presence of aluminum chloride to produce aniline which was obtained, however, in small amounts.

Frankforter and co-workers in 1914 (14) reported in a series of articles that they had successfully condensed chloral, chloral hydrate, bromal, and tri-oxymethylene with various organic compounds in which there was an elimination of water. They could not obtain all the products by the Baeyer or sulfuric acid reaction, thus Frankforter maintained that aluminum chloride acts primarily as a catalyst and at the same time plays the part of a dehydration agent.

Prins (15) in 1927 gave some concepts on the mechanisms of aluminum chloride condensation. He stated that benzene under the influence of aluminum chloride acted as if it had a mobile hydrogen linkage apparently has undergone ionization under the influence of aluminum chloride's strong positive ion. Dougherty (16) agreed mainly with Prins but believed in an addition compound between benzene and aluminum chloride with the hydrogen loosely held. Wohl and Werlzporoch (17) were of the same opinion. However, one should not overlook the dehydrative power no matter what its catalytic action is toward aromatic compounds.

Huston and Friedmann (18) were the first to employ aluminum chloride as a condensation reagent to the aromatic alcohols. They obtained diphenylmethane as the principle product in the treatment of benzyl alcohol with benzene. The yields of the final product and by-product were found to be a function of the temperature and amounts of reagents used. Later they extended their work (19) to secondary alcohols with benzene and aluminum chloride using methylphenylcarbinol, ethylphenyl carbinol and benzhydrol obtaining diphenylethane, diphenylpropane and triphenylmethane respectively. A much higher yield and smoother reaction was obtained from the methylphenyl carbinol than from the ethylphenyl carbinol which led them to conclude that the ethyl group had a greater retarding effect than did the methyl group.

Huston (20) extended his work when he condensed benzyl alcohol with phenol in the presence of aluminum chloride obtaining parabenzylphenol. Good yields of the methylethyl ethers were obtained upon condensing benzyl alcohol with anisols and phenetol. Thereby showing that the phenolic hydroxyl group did not interfere with the substitution of the benzyl group into the benzene ring.

Huston and Bartlet (21) condensed phenylbutyl carbinol and phenol to give p-hydroxyl 1, 1 diphenylpentane. The hypothesis that unsaturation of carbon atoms adjacent to the alcoholic group increases the reactivity of the hydroxyl group was confirmed by the large yield of p-hydroxytriphenylmethane.

Huston, Lewis, and Grotemut (22) obtained p-hydroxy 1, 1 diphenylpropane, and p-hydroxytriphenylmethane by condensation. p-Hydroxy 1, 1 diphenylbutane was added to this list later by Huston and Stickler (23).

Huston and Sager (24) reported at that time that methyl, ethyl, iso-propyl, butyl, iso-butyl, and iso-amyl alcohols would not condense with benzene in the presence of aluminum chloride. However, by a modification of the former's procedure Hsieh (25) did condense iso-propyl, iso-butyl, and iso-amyl (but not the normal) alcohols with benzene. Huston and Fox (26) condensed tert-butyl alcohol, tert-amyl alcohol, dimethyl n-propyl carbinol and dimethyl iso-propyl carbinol with benzene in the presence of aluminum chloride to form tert-butylbenzene, tert-amylbenzene, dimethyl n-propylphenylmethane, and dimethyl iso-propylphenylmethane in good yields.

Huston and Binder (27) prepared several heptyl benzenes by this method. The alcohols used were dimethyl n-butyl carbinol, dimethyl iso-butyl carbinol, dimethyl sec-butyl carbinol, methylethyl n-propyl carbinol, methylethyl iso-propyl carbinol, and triethyl carbinol which were condensed with benzene giving good yields of the alkyl benzene.

Hradel (28) was reported to have had no condensation of diphenylethyl or diphenylpropyl carbinols with benzene in the presence of aluminum chloride. Instead there was noted a great tendency for the splitting off of a molecule of water from the carbinol to form an unsaturated hydrocarbon. Fox (29) reported no condensation of diethylphenyl carbinol. The inability of these latter carbinols to condense may be explained by the fact that the OH group is drawn closely to the carbon atom thereby inhibiting it from being split off.

Macomber (30) attempted to condense diethylphenyl carbinol, dimethylphenyl carbinol, and methylethylphenyl carbinol with benzene in the presence of aluminum chloride to give the corresponding hydrocarbon. Methylethylphenyl carbinol and dimethylphenyl carbinols did give the predicted hydrocarbons but the diethylphenyl carbinol did not condense with benzene.

Huston and Sculati (31) condensed dimethylamyl carbinols (n-amyl, active amyl and sec-amyl) with benzene in the presence of aluminum chloride to form the alkyl benzene and also found that the branched chain carbinols showed decreasing readiness to condense with benzene as the branching approached the carbinol group.

Huston and Breining (32) in 1938 reported good yields when they condensed diethyl n-propyl carbinol and diethyl iso-propyl carbinol with benzene in the presence of aluminum chloride to give diethyl n-propylphenylmethane and diethyl iso-propylphenylmethane.

Huston and Guile (33) reported having obtained condensation products of 2-methylheptanol-2, 2, 3-dimethylhexanol-2, 2,3,3-trimethylpentanol-2, 2,4-dimethylhexanol-2, 2,5-dimethylhexanol-2 2,3,4-trimethylpentanol-2, and 2,4,4-trimethylpentanol-2 with phenol in the presence of aluminum chloride. The yields of the resulting p-t-alkylphenols ranged from 2.1 to 69.5 per cent.

PREPARATION OF CARBINOLS

Methyl di n-propyl carbinol

Methyl di n-propyl carbinol was first prepared in 1886 by Gortalow and Saytzeff (34) when they reacted butyron and methyl iodide in the presence of zinc to give the desired carbinol in a 30 per cent yield. Later Halse (35) prepared the same carbinol by treating n-propyl magnesium bromide with ethyl acetate. It was also prepared by Stadnikow (36) when he used benzhydryl acetate and n-propyl magnesium bromide to give a 40 per cent yield.

Preparation of Grignard reagent

Into a 3-liter 3-necked round bottomed flask equipped with a glycerine sealed stirrer, a reflux condenser and dropping funnel was placed 50 gms (2.06 moles) of dry magnesium turnings and one hundred ml. of anhydrous diethyl ether. To this was added a mixture of 246 gms (2 moles) of the halide (n-propyl bromide) and 500 ml. of anhydrous diethyl ether. A small amount of the mixture was run into the flask through the separatory funnel to start the reaction; the reaction was continued by the addition of the rest of the mixture at the rate of one drop per second or less.

Preparation of the carbinol

To the Grignard reagent 88 gms (1 mole) of freshly distilled ethyl acetate was added at a rate such that the ether refluxed gently. Stirring was continued for two hours after the last of the ethyl acetate had been added.

After standing overnight the mixture was hydrolyzed by pouring the contents of the flask onto ice and treating the resulting mixture with reagent hydrochloric acid until the water layer became clear.

The ether-water layers were separated by the use of a separatory funnel and the water layer was extracted three times with ether. The ether extracts were combined and anhydrous sodium sulfate was added and allowed to set overnight to dry.

The ether was distilled off on a water bath and the product was subjected to a distillation under reduced pressure. Methyl di n-propyl carbinol was collected between 52 - 53.5°C. at 3.5 mm.

Methyl n-propyl iso-propyl carbinol

It was first prepared by Clarke in 1911 (37) when he added 2-methyl 3-butanone to the Grignard reagent, n-propyl magnesium bromide, to give a 45 per cent yield of the carbinol.

Preparation of Methyl n-propyl iso-propyl carbinol

To the Grignard reagent was added 172 gms. (2moles) of methyl iso-propyl ketone. The rate of addition was such that the ether refluxed gently. The stirring was continued two hours after the last of the methyl iso-propyl ketone had been added. The resultant product was hydrolyzed in the usual manner.

Methyl n-propyl iso-propyl carbinol was collected between 44.5 - 46.5°C. at 3.5 mm pressure.

Methyl di iso-propyl carbinol

Methyl di iso-propyl carbinol was prepared in 76 per cent yields from di iso-propyl ketone and methyl magnesium chloride by Whitmore and Laughlin (38) in 1932.

Preparation of Methyl magnesium bromide

The methyl bromide generator (by a modification of the procedure given for methyl chloride (39))consists of a 3-liter 3-necked round bottom flask resting on a sand bath and fitted with a reflux condenser with a delivery tube running from the top of the condenser to a train of wash bottles, three containing a saturated solution of sodium hydroxide, three containing conc. sulfuric acid, and three safety bottles (one at each end of the train and one between the sodium hydroxide and the conc. sulfuric acid bottle). It was charged for a 12 mole (theoretical) of methyl bromide. 53 gms of water and 586 gms (320 cc.) of conc. sulfuric acid are placed in the flask and 370 gms (470 cc.) of methyl alcohol is added, with cooling, at such a rate that the temperature does not rise above 70°C. Then 1130 gms of sodium bromide is added, the apparatus is tightly connected, and the flask heated on the sand bath so that the gas is evolved at a fairly rapid rate. It has been found in practice that, using materials of the commercial grade, the yield of methyl bromide is about 55 - 65 per cent of the theoretical amount. The methyl bromide is passed through the wash bottles into a 3-1 3-necked round bottom flask into which 75 gms (3.09 moles) of magnesium, a few crystals of iodine, some ethyl bromide to start the reaction and 600 ml of anhydrous di ethyl ether have been placed. The reaction takes place smoothly - taking about two hours to use up the magnesium. The reaction was carried out under the hood as the methyl bromide is a poisonous gas.

To the Grignard reagent was added 296 gms (370 cc.) of di iso-propyl ketone in 400 cc. of anhydrous di ethyl ether. It was added at such a rate that the ether refluxed gently. The resultant product was hydrolyzed as instructed under methyl di n-propyl carbinol.

Methyl di iso-propyl carbinol was collected between 53 - 54°C. at 13 mm. pressure.

CONDENSATIONS

Condensations

General Procedure:

A 500 ml 3-necked round bottom flask was provided with a glycerine sealed mechanical stirrer, a reflux condenser with a thermometer inside, and a separatory funnel. Benzene (5 equiv.) was placed in the flask and the stirrer was started. The entire amount of aluminum chloride (1/2 equiv.) was added to the benzene and uniformly suspended in the benzene. The carbinol (1 equiv.) was added by means of the separatory funnel, fitted with a $CaCl_2$ tube, at a rate of 1 drop every 3 or 4 sec. so that the temperature didn't rise above 30°C. A considerable amount of hydrochloric acid fumes were evolved during the process of the addition of the carbinol. If the temperature went above 30°C. it was cooled by means of a ice bath, the temperature remained between 25 - 30°C. The mixture was stirred for 4 hours after the last of the carbinol had been added. It was allowed to stand overnight and then decomposed by ice and reagent HCl. The benzene layer was separated and the water layer was extracted three times with ether, the benzene ether layer was then washed with sodium carbonate to remove any excess acid and allowed to dry overnight over anhydrous sodium sulfate. The ether and benzene were distilled off from a water bath and the remaining solution was distilled under reduced pressure.

Methyl di n-propyl carbinol, benzene and aluminum chloride

Following the above procedure the following amounts were used:

Run #1	grams	Equivalents	Moles
Carbinol	32.0	1	1/4
Benzene	97.5	5	1 1/4
Aluminum chloride	16.6	1	1/4

The following fractions were obtained:

Up to 112°C. - -	12 mm	5 gms
112 - 115°C. - -	12 mm	12 gms
Above 115°C. - -	12 mm	7 gms

The second fraction was redistilled and purified and finally collected between 109 - 111°C. at 10 mm. (oil bath at 134 - 139°C.) and was found to be 4-methyl 4-phenylheptane. The boiling point at 749 mm. was found to be 242 - 243°C. Yield 25.7 per cent.

On the second trial a 1/2 mole run was made which gave about a 10 per cent higher yield. Yield 37.9 per cent.

4-methyl 4-phenylheptane was prepared originally by Halse (40) from 4-chloro 4-methylheptane and benzol in the presence of aluminum chloride. Later it was prepared by the same author by the reduction with H_2 in the presence of black platinum in glacial acetic acid of methyl γ cylobenzylheptane (41).

Methyl n-propyl iso-propyl carbinol, benzene and aluminum chloride

Following the general procedure the following amounts were used:

Run #1	Grams	Equivalents	Moles
Carbinol	32.0	1	1/4
Benzene	97.5	5	1 1/4
Aluminum chloride	16.6	1	1/4

The following fractions were obtained:

Up to 102°C.	11 mm	11 gms
102 - 107°C.	11 mm	8.4 gms
Over 107°C.	11 mm	5 gms

Yield 18 per cent

The second fraction was redistilled and purified and finally collected between 104.5°C. - 106.5°C. at 11 mm and was found to be 2,3-dimethyl 3-phenylhexane. The boiling point at atmospheric pressure was 237 - 238°C. at 748 mm.

On the second trial a 1/2 mole run was made which gave about the same yield. Yield 18.8 per cent.

Methyl di iso-propyl carbinol, benzene and aluminum chloride

A modification was made in the general procedure due to the formation of bi products in that procedure.

The benzene and aluminum chloride were suspended in petroleum ether and the contents cooled to a minus 30°C. The carbinol was then added at such a rate that there was no noticeable change in temperature. In trial number one after the alcohol had been added the product was allowed to warm up at room temperature while in trial number two it was placed in the ice box for 24 hours and then allowed to come to room temperature. It was decomposed and treated as under the general procedure.

Run#1	Grams	Equivalents	Moles
Carbinol	64.0	1	1/2
Benzene	60.0	3	3/4
Aluminum chloride	33.0	1	1/2

The following fractions were obtained:

Up to 108°C.	-- 14 mm	34 gms
108 - 115°C.	-- 14 mm	4 gms
Over 115°C.	-- 14 mm	9 gms

The second fraction was redistilled and purified and finally collected between 104 - 106°C. at 13 mm. (oil bath 134 - 136°C,) and was found to be 2,3,4-trimethyl 3-phenylpentane. The boiling point at atmospheric pressure was 234 - 236°C. at 743 mm. Yield 4.33 per cent.

On the second trial a 1/2 mole was also ran and a 7.57 per cent yield was obtained.

The low fractions were combined and a chloride was distilled over which was found to be 3-chloro 2,3,4-trimethylpentane which boiled between 53 - 56°C. at 14 mm.

DATA AND PHYSICAL CONSTANTS

Determination of Physical Constants

The density was determined by using a small pycnometer. The weighings were all made at 20°C. and compared with water at 4°C.

Measurements of the index of refraction were made on a Abbe refractometer.

A Du Nouy Tensiometer was used to determine the surface tension. A standardization of the instrument was necessary which was accomplished by means of the following ~~equation~~ factor:

$$\frac{\text{wt. of Cu wire} \times 981}{2 \times 4 \times \text{dial reading}}$$

The molecular refractions were calculated by using the Lorenz-Lorentz formula:

$$M_D = M/d \times \frac{n^2 - 1}{n^2 + 2}$$

M_D = Molecular refraction

M = Molecular weight

d = Density

n = Index of refraction

The theoretical molecular refractions were calculated from the following atomic refractions:

(Zeitschrift Physicalische Chemie, 7, 140, (1891)

C–H = 1.705

C–C = 1.209

C = 2.418

H = 1.100

Double bond = 1.733

The observed parachor was calculated by the formula:

$$P = M/d \; x \; \gamma^{\frac{1}{4}}$$

Where: P = Parachor of compound

M = Molecular weight

d = Density

$\gamma^{\frac{1}{4}}$ = Surface tension

The molecular weights were obtained by observing the lowering of freezing point. The solvent was pure benzene into which the compounds were placed.

DATA SHEET

Compound	B. P. Obtained		B. P. Reported		Percent Yield	Index Refraction at 20°C	Du Nouy Sur. Tens. at 20°C	$D^{20°}_{4°}$
	Reduced Pressure	Atmos. Pressure	Reduced Pressure	Atmos. Pressure				
Methyl di n-propyl carbinol	62 - 63/ / 12mm	157 - 159/ /748.5mm	61 - 63/ / 12mm	159 - 161/ /755 mm	52 - 66	1.4258	26.675	0.8208
Methyl n-propyl iso-propyl carbinol	54 - 56/ / 13 mm	155.5-157.5/ /748.5mm		158 - 158.2/ /760 mm	33 - 38.7	1.4317	27.500	0.8344
Methyl di iso-propyl carbinol	53 - 54/ / 13 mm	146 - 147/ /740.5mm	75 - 77/ / 40 mm		76 - 86	1.4342	28.325	0.8457
4-methyl 4-phenyl-heptane	109-111/ / 10 mm	242 - 243/ /749 mm	120 - 121/ / 12 mm		25.7-37.9	1.4930	31.18	0.8700 ? 8676
2,3-di methyl-3-phenylhexane	104.5-106.5/ / 11 mm	237 - 238/ /748 mm			18 - 18.8	58 1.4900	132 30.80	7 0.8663
2,3,4-trimethyl-3-phenylpentane	104 - 106/ / 13 mm	234 - 236/ /743 mm			4.33-7.57	70 1.4968	4 31.763	0.8808

DATA SHEET

Compound	Carbon & Hydrogen Det.		Molecular Weight	Molecular Refraction		Parachor	
	Theoretical	Obtained		Theoretical	Calculated	Calc.	Du Nouy
4-methyl 4-phenyl-heptane	C 88.33% H 11.67%	C 88.34% H 11.64%	190.88	25 63.25	4 63.57	522.4	518.25
2,3-di methyl 3-phenylhexane	C 88.33% H 11.67%	C 88.43% H 11.68%	189.92	63.25	44 63.51	513 519.4	12.5 517.52
2,3,4-trimethyl-3-phenylpentane	C 88.33% H 11.67%	C 88.55% H 11.51%	189.72	63.25	63.18	516.4	11.2 513.0

SUMMARY

Summary

1. The methyl dipropyl carbinols condensed with benzene in the presence of aluminum chloride.

2. The physical constants were determined for each condensation compound.

REAGENTS USED

Reagents Used

iso-Propyl Bromide: Prepared by adding 48 per cent HBr to iso-propyl alcohol in the presence of Conc. H_2SO_4 and refluxing. Yield 75 - 80 per cent.

n-Propyl Bromide: Prepared by adding 48 per cent HBr to n-propyl alcohol in the presence of Conc. H_2SO_4 and refluxing for several hours. Yield 70 per cent.

Ethyl Acetate: Baker's U.S.P. from the stockroom.

Methyl iso-Propyl Ketone: Prepared by brominating tert.-amyl alcohol and hydrolyzing to obtain the desired product. (42) Yield 55 - 70 per cent.

Magnesium: Fresh magnesium turnings were obtained from the stockroom and were placed in a desiccator over $CaCl_2$ until ready for use.

Anhydrous di Ethyl Ether: This was obtained from the stockroom and allowed to stand over fresh cut metallic sodium until ready for use.

Benzene: Thiophene free benzene (C.P.) was obtained from the stockroom and allowed to stand over fresh cut metallic sodium until ready for use.

Anhydrous Aluminum Chloride: (Tech.) This was obtained from the stockroom.

Di iso-Propyl Ketone: (Pract.) Was obtained from Eastman. It was redistilled and collected over a two degree range.

Petroleum Ether: (C.P.) Obtained from stockroom and was dried over $CaCl_2$ until ready for use.

Anhydrous Sodium Sulfate: This was obtained from the stockroom and was of a good quality.

Sodium Bromide: Obtained from the stockroom and was of a commercial grade.

Methyl Alcohol: Was obtained from stockroom.

BIBLIOGRAPHY

Bibliography

(1)	Lewis and Kossel	J. Am. Chem. Soc., 46, 137, (1924)
(2)	Fisher and Roser	Ber., 13, 674
(3)	Becker	Ber., 15, 2090
(4)	Meyer and Wurster	Ber., 6, 964
(5)	Micheal and Jeanpretre	Ber., 25, 1615
(6)	Hemilian	Ber., 16, 2360
(7)	Mazzara	Gazz. Chim. Ital., 12, 505
(8)	Noelting	Ber., 24, 553
(9)	Rhotinski, Patzewitch	Ber., 24, 3104
(10)	Friedel and Craft	Comp. Rend., 84, 1392
(11)	Mers and Weith	Ber., 14, 187
(12)	Wass	Ber., 15, 1128
(13)	Graebe	Ber., 34, 1778
(14)	Frankforter and coworkers	J. Am. Chem. Soc., 36, 1911 37, 385
(15)	Prins	Chem. Weekblad., 24, 615
(16)	Dougherty	J. Am. Chem. Soc., 51, 576
(17)	Wohl and Werlsporoch	Ber., 64, 1357
(18)	Huston and Friedmann	J. Am. Chem. Soc., 38, 2527
(19)	Huston and Friedmann	J. Am. Chem. Soc., 40, 785
(20)	Huston	J. Am. Chem. Soc., 40, 2775
(21)	Huston and Bartlet	(Master's Thesis 1926)
(22)	Huston, Lewis, and Grotemut	J. Am. Chem. Soc., 49, 1365
(23)	Huston and Sticker	J. Am. Chem. Soc., 55, 4317

(24) Huston and Sager	J. Am. Chem. Soc., 48, 1955
(25) Huston and Hsieh	(Doctor's Thesis 1935)
(26) Huston and Fox	(Master's Thesis 1934)
(27) Huston and Binder	(Master's Thesis 1935)
(28) Huston and Hravel	(Master's Thesis 1934)
(29) Huston and Fox	(Bachelor's Thesis 1933)
(30) Huston and Macomber	(Master's Thesis 1935)
(31) Huston and Sculati	(Master's Thesis)
(32) Huston and Breining	(Master's Thesis 1938)
(33) Huston and Guile	J. Am. Chem. Soc., 61, 69 (1939)
(34) Gortalow and Saytzeff	J. prakt. Chem. 33, 203
(35) Halse	J. prakt. Chem., 89, 453
(36) Stadnikow	Ber., 47, 2137
(37) Clarke	J. Am. Chem. Soc., 33, 528
(38) Whitmore and Laughlin	J. Am. Chem. Soc., 54, 4392
(39) Organic Synthesis	Vol. X, 36
(40) Halse	J. prakt. Chem., 89, 453
(41) Halse	J. prakt. Chem. 92, 44
(42) Organic Synthesis	Vol. XIII, 68