THE REACTION OF ALPHA-HALOGEN ACID HALIDES WITH GRIGNARD REAGENTS

I. THE REACTIONS OF ALPHA-BROMOACETYL BROMIDE AND ALPHA-CHLOROACETYL CHLORIDE WITH METHYL AND ETHYL-MAGNESIUM BROMIDES AND IODIDES

Thesis for the Degree of M. S.
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by

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Introduction

In conjunction with the work being done in this laboratory on the preparation and condensation of alcohols with phenol, benzene and their derivatives, the reaction of alpha-halogen acid halides with Grignard reagents was investigated as a possible means of preparing some of the branched, tertiary alcohols.

If the reaction were to proceed in the expected manner, it would yield, upon hydrolysis, a tertiary alcohol, the halogen in the alpha position of the acid halide being replaced by the alkyl radical of the Grignard reagent. This was not found to be the case. Instead of a tertiary, a secondary alcohol was obtained.

This thesis will give a description of the different reactions carried out. It will also attempt to explain the deviation of the reaction from the expected course by proposing a reaction mechanism.

HISTORICAL

Historical

To the author's knowledge, this paper represents the original work done on the reaction of Grignard reagents with alpha-halogen acid halides. The search in the literature revealed that no such reaction has been carried out previously. The historical portion of this thesis will, therefore, give a brief discussion of the work carried out in related fields; namely, the hydrocarbon synthesis, the reaction of Grignard reagents with acid halides, the reaction of Grignard reagents with alpha-halogen compounds, and the reaction of Grignard reagents with dialkyl zinc.

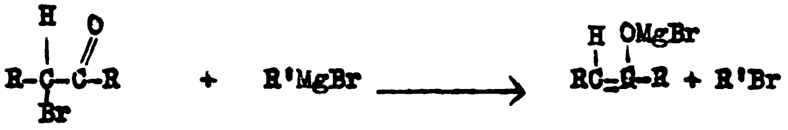
The hydrocarbon synthesis by use of a Grignard reagent and an alkyl halide has long been known and has been widely employed. In 1913, Späth (1) published a comprehensive paper dealing with the reactions of a large number of alkyl halides with Grignard reagents. He found that the yields of the desired hydrocarbons were usually low, and that other hydrocarbons were produced. This led him to the conclusion that alkyl radicals were first produced by the reaction, and that the subsequent combination of those radicals gave rise to the variety of hydrocarbons. Previous to Späth, in 1903, Houben (2) found that unless RMgX and R'X were heated together, the hydrocarbon R-R' would not be formed. In 1906, Gomberg and Cone (3) prepared Ph_3C-CH_2Ph in good yields from benzylmagnesium chloride and triphenylchloromethane.

Trotman (4) in 1925, tried to prepare quaternary compounds of the type $(C_6H_5CH)_2CR_1R_2$ by the reaction of Grignard reagent with tertiary halogen derivatives. His success was somewhat limited. Carothers and Burchet (5) were able to prepare phenyl-4-butadiene 1,2 from chloro-4-butadiene 1,2 and phenylmagnesium bromide. Mitchovitz (6) in 1935, in order to show the stability of the five-membered ring, reacted o-chlorocyclopentanone with methyl, ethyl, propyl and phenyl Grignards. In all cases the chlorine was replaced by the alkyl of the Grignard.

The reaction between acid halides and Grignard reagents has been used to prepare tertiary alcohols. Gilman and Fothergill (7) were able to prepare tertiary alcohols in as high yields as 93%. Gilman and Mayhue (8) reported the effect of varying the amounts of the Grignard reagent. They reacted benzoyl chloride with phenylmagnesium iodide and found that if the reactants were used mole for mole, the product was benzophenone. If an excess of the Grignard reagent was used, the product was mainly triphenylcarbinol. They further reported that the yield of ketone was affected by the halogen present in the Grignard reagent in the order I >Cl >Br.

Some work has been done recently on the reaction of Grignards with alpha-halogen compounds. In 1930 Fisher (9) found that the alpha halogen in some alpha-halo-ketones was repaced by the hydrogen under the influence of a Grignard reagent. He found that if benzoyldiphenylmethyl bromide were reacted with PhMgBr, the product upon hydrolysis was benzoyldiphenyl methane. He explained the reaction through the formation of unsaturated intermediate compounds, which upon hydrolysis gave the compound with hydrogen in place of the halogen.

Kohler and Tishler (10) found that if an alpha-bromoketone were reacted with one mole of Grignard reagent, the product was an unsaturated compound and an alkyl halide formed by combination of the alkyl from the Grignard reagent and the alpha-halogen. They expressed the reaction as follows:



$$R-\underset{Br}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-R \quad + \quad R'MgBr \longrightarrow R\overset{\overset{H}{|}}{C}=\overset{\overset{OMgBr}{|}}{C}-R + R'Br$$

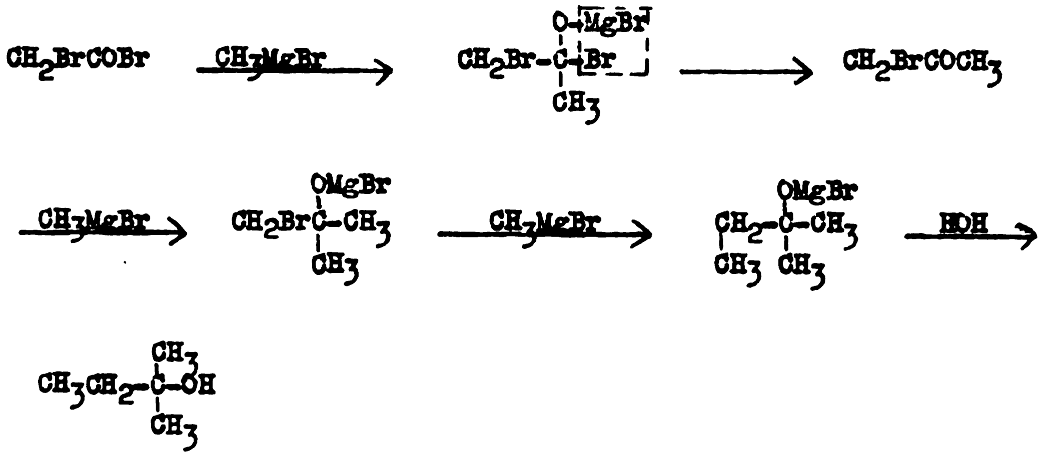
Aston (11) working with alpha-halo nitroso compounds and Grignard reagents found that an unsaturated compound was produced. None of these workers used an excess of Grignard reagent.

The only work done which is closely related to that of this thesis was done by Winogradow (12) in 1878. He reacted one mole of alpha-bromoacetyl bromide with three moles of zinc dimethyl. The product he obtained was methylisopropyl carbinol. When zinc diethyl was used, 4-ethyl hexanol-3 was obtained. He explains the mechanism of the reaction by assuming a rearrangement to have occurred.

Theoretical and Discussion

In all of these reactions, the ratio of alpha-halogen acid halide to the Grignard reagent was 1 : 3.5. Three moles of Grignard reagent were used as the calculated amount and a half mole was used as an excess.

If the reaction were to proceed in the manner expected, the product would be a tertiary alcohol.

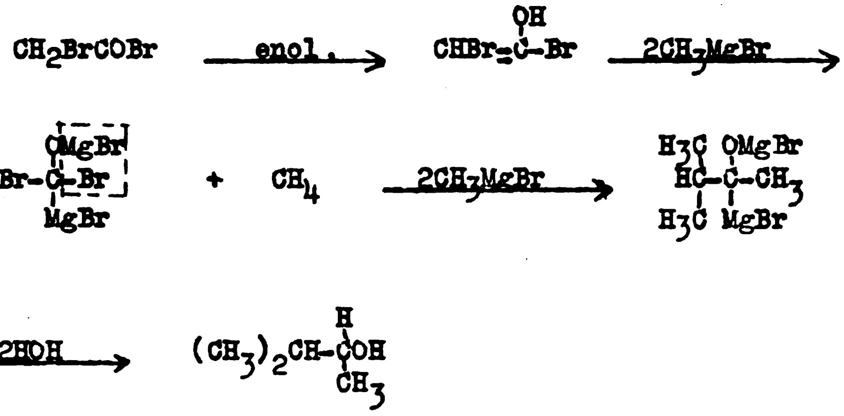


$$CH_2BrCOBr \xrightarrow{CH_3MgBr} CH_2Br\text{-}\overset{O-MgBr}{\underset{CH_3}{C}}\text{-}Br \longrightarrow CH_2BrCOCH_3 \xrightarrow{CH_3MgBr} CH_2Br\overset{OMgBr}{\underset{CH_3}{C}}\text{-}CH_3 \xrightarrow{CH_3MgBr} \underset{CH_3}{CH_2}\text{-}\overset{OMgBr}{\underset{CH_3}{C}}\text{-}CH_3 \xrightarrow{HOH} CH_3CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OH$$

The first mole of the Grignard reagent would react with the acid halide group and split off $MgBr_2$ (13) to give bromoacetone. The second mole of Grignard would react normally with the carbonyl group, and the third mole would react with the alpha-halogen, splitting off $MgBr_2$ and putting in a CH_3 group. The final product upon hydrolysis would be tertiary amyl alcohol. This alcohol was not found to be the product. A secondary alcohol was obtained, methyl isopropyl carbinol. That the course of the reaction did not proceed as expected was further shown by the fact that a secondary octyl alcohol, 4-ethyl-hexanol-3, was obtained when ethylmagnesium bromide was used.

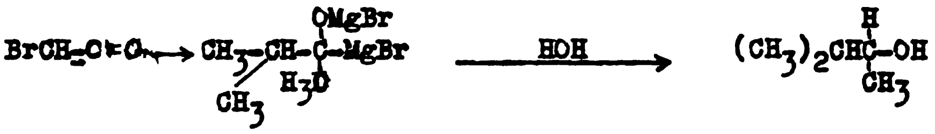
In order to explain the deviation of the reaction from the expected course, two possible courses of reaction are given.

(A)



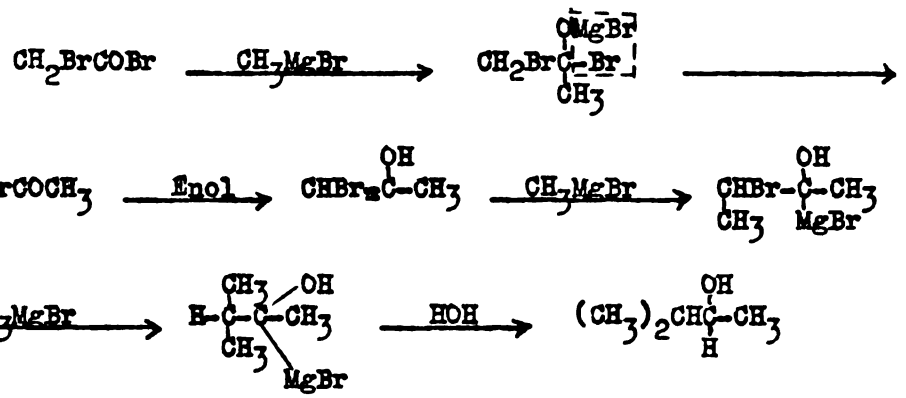
In this reaction, the bromoacetyl bromide is assumed to enolize under the influence of the Grignard reagent (14). Two moles of Grignard reagent then react, one with the active enol hydrogen (15) and one with the double bond. The next two moles react respectively with the carbonyl group formed and with the alpha-hydrogen. The final product upon hydrolysis will be methylisopropyl carbinol.

It is also possible that the unstable enolization product might split off HBr to give a brominated ketene. If the ketene were to react with three moles of Grignard reagent, the product would be methylisopropyl carbinol.



The first mole of Grignard reagent reacts with the carbonyl group, the second mole with the double bond, and the third mole with the alpha halogen. No HBr was observed to be given off during the course of the reaction. Also, it will be observed that four moles of Grignard reagent were necessary to carry the reaction to completion. This is possible due to the fact that excess Grignard reagent was used.

(B)



In this reaction, bromoacetone produced by the reaction of one mole of CH_3MgBr is assumed to undergo enolization (16), (17). The second mole reacts with the double bond, and the third mole replaced the alpha halogen. If the second mole were to react with the active enolic hydrogen, four moles would be needed to complete the reaction, and the product would still be methylisopropyl carbinol. Due to the fact that the yields were low and that excess Grignard reagent was used, it is possible that the reaction proceeded in the ratio of one mole of bromoacetyl bromide to four moles of methylmagnesium bromide.

In an effort to establish the mechanism of the reaction, attempts were made to isolate one of the intermediate products. Such attempts were unsuccessful, the difficulty being the tendency of the intermediate products to polymerize. If reaction (A) represented the correct mechanism, the reaction product of two moles of methylmagnesium bromide and bromoacetyl bromide upon hydrolysis should be alpha-bromopropionaldehyde. This in itself polymerizes. If it lost HBr, acrylic aldehyde, which polymerizes very readily, would be formed. Neither the bromoaldehyde nor acrylic aldehyde were isolated.

If reaction (B) represented the true mechanism, then the product of bromoacetyl bromide and one mole of methylmagnesium bromide would be bromoacetone. A small fraction was isolated in the range of bromoacetone, but it failed to yield a derivative. This fraction had the irritating effect on the eyes common to bromoacetone. The fraction polymerized readily (18).

Since bromoacetone could not be isolated as an intermediate, it was decided to prepare it by a known method and react it with methylmagnesium bromide. This was carried out (as described in experimental) and the product obtained was methyl isopropyl carbinol.

The fact that methylisopropyl carbinol was obtained from bromoacetone and methylmagnesium bromide indicates that the probable mechanism of the reaction is that shown in (B).

EXPERIMENTAL

MATERIALS USED

1. Chloroacetic acid, m.p. 62-64, Central Scientific
2. Phosphorus trichloride, Pract.
3. Sodium bromide
4. Methyl abchol, Pract. Merck
5. Sulfuric acid, conc., C.P.
6. Methyl iodide, B.P. 41-43°, Eastman
7. Ethyl bromide, B.P. 38-40°, Dow Chem.
8. Anhydrous Ether (kept over sodium)
9. Acetic acid, glacial, C.P.
10. Acetone, C.P., Merck
11. Bromine
12. Red Phosphorous
13. Diethyl carbinol, B.P. 114-116°, Eastman
14. n-Propyl alcohol, B.P. 96-98°, Eastman
15. Potassium dichromate
16. Hydrochloric acid, C.P.
17. Magnesium turnings
18. Ethyl ester of chloroacetic acid, prepared in this laboratory, B.P. 140-143°.
19. Methylisopropyl carbinol, B.P. 110-113°, Eastman

Preparation of Reactants

Chloroacetyl chloride (19)

In a 5-liter, three-neck, round bottom flask, fitted with a glycerine sealed stirrer, reflux condenser and dropping funnel, was placed 756 gms. (8 moles) of chloroacetic acid. The flask was warmed until the chloroacetic acid melted. The stirrer was started and 415 gms. (3 moles) of phosphorous trichloride was added drop by drop. The addition required about one hour, after which time the reaction mixture was allowed to stand in the flask for two hours. The liquid portion was decanted from the phosphorous acid and the white solid formed on the sides of the flask, and was fractionated. The fraction boiling at 103-106° was taken. Yield, 370 gms.

Bromoacetyl bromide (19), (20)

This compound was prepared in two steps. First, the acetyl bromide was prepared and then the alpha position was brominated.

In a 5-liter, three-neck, round bottom flask fitted with a glycerine sealed stirrer, a reflux condenser, and dropping funnel was placed 600 gms. (10 moles) of glacial acetic acid. The stirrer was started, and 750 gms. (3.75 moles) of PBr_3 was added dropwise. The reaction mixture was allowed to stand for two hours. The acetyl bromide was decanted from the phosphorous acid and fractionated. The fraction boiling 70-80° was collected.

The acetyl bromide prepared above was placed in a 3-liter, three-neck round bottom flask, fitted with a glycerine sealed stirrer, a reflux condenser, and a dropping funnel. To this was added 5 gms. of red phosphorus. The stirrer was started, and 1300 grms. of bromine was added through the dropping funnel. The addition required three hours. The reaction mixture was allowed to stand overnight. The flask was then gently heated until all excess bromine had been given off. The mixture was fractionated and 1150 gms. of bromoacetyl bromide was collected, boiling at 146-149°.

Bromoacetone

Bromoacetone was prepared by brominating acetone with bromine in the presence of acetic acid (21). The bromoacetone must be used as soon as possible, or refrigerated. It was found that if bromoacetone were allowed to stand at room temperature, it blackened. Upon refractionation, the product could not be obtained, in its original state of purity, and on reaction with methyl magnesium bromide, it did not give the desired product.

Preparation of Grignard Reagents

Methylmagnesium iodide and ethylmagnesium bromide were prepared in the usual manner, e.g., the calculated amount of alkyl halide in anhydrous ethyl ether was added to magnesium turnings in a three-neck, round bottom flask, fitted with a glycerine sealed stirrer, reflux condenser and dropping funnel. The rate of addition was such that the reaction mixture refluxed gently.

Methylmagnesium bromide was prepared by passing methyl bromide gas into a mixture of magnesium in anhydrous ether. Methyl bromide was prepared by heating a mixture of sodium bromide, methyl alcohol and concentrated sulfuric acid (22). The gas was passed through a battery of wash bottles containing 30% sodium hydroxide and concentrated sulfuric acid. The base was used to neutralize any HBr that might have formed, and the acid was used to dry the methyl bromide gas.

In a 3-liter, three-neck, round bottom flask fitted with a glycerine sealed stirrer, a reflux condenser, and a methyl bromide delivery tube was placed 97 gms. (4 moles) of magnesium turnings. The flask was warmed, and 2 cc. of methyl iodide was added. To this was added about 20 cc. of anhydrous ether. As soon as the initial reaction had subsided, the stirrer was started, and 2 liters of anhydrous ether was added. Methyl bromide was allowed to pass in at such a rate that the reaction mixture refluxed gently. The reaction mixture darkened in the course of two to three hours. The reaction was complete when all of the magnesium had reacted. This required from 10 to 15 hours. The reaction was found to be about 90% efficient (by titration), so that for every four moles of magnesium used, there was formed 3.5 moles of Grignard reagent.

Reactions Proper

Reactions of $CH_2XCOX + 3.5\ RMgX$

The following reactions of this type were carried out. The results are shown in the Table of Results.

1. Chloroacetyl chloride + methylmagnesium bromide
2. Chloroacetyl chloride + methylmagnesium iodide
3. Chloroacetyl chloride + ethylmagnesium bromide
4. Bromoacetyl bromide + methylmagnesium bromide
5. Bromoacetyl bromide + methylmagnesium iodide
6. Bromoacetyl bromide + ethylmagnesium bromide

Also the ethyl ester of chloroacetic acid was reacted with methylmagnesium bromide.

Since the same procedure was used in carrying out all of the above reactions, only one run will be described.

In a 3-liter, three-neck, round bottom flask, fitted with a reflux condenser, stirrer, and dropping funnel, 3.5 moles of methylmagnesium iodide were prepared as described above. To this was added, dropwise, 113 gms. (1 mole) of chloroacetyl chloride in 500 cc. of anhydrous ethyl ether. The reaction was very violent, and addition was slow. The reaction mixture turned to a yellowish color and finally darkened.

After all of the chloroacetyl chloride had been added, the reaction mixture was allowed to stand in the flask for about one hour. The flask was then removed and placed on the steam bath. A condenser was fitted to the flask so that a downward distillation would be accomplished. The steam bath was gradually turned on until all of the ether in the reaction flask had distilled over. The steam bath was then turned on completely and the contents of the reaction flask were allowed to bake for 24 to to 36 hours. At the end of this time, the contents of the flask were a yellowish, brittle solid.

The solid was removed and hydrolized with ice and concentrated hydrochloric acid. Enough acid was used to disperse the precipitate of magnesium hydroxide. The hydrolized mixture divided into two layers. The top layer was separated out, and the lower layer was extracted three times with ether. The ether extracts were mixed with the top layer and dried over a mixture of anhydrous sodium sulfate and sodium carbonate. The ether was then removed and the product was fractionated. The portion coming over at 109-112° was taken as the main fraction. This was later identified as methylisopropyl carbinol.

In all cases where methyl Grignard was used, a small, low-boiling fraction was obtained, but no high fractions. In the case of ethyl Grignards, both low and high fractions were present. The main fraction came over at 43-45° at 4 mm. of pressure. This was found to be 4-ethylhexanol-3.

Bromoacetyl bromide + 1 methylmagnesium bromide and bromoacetyl bromide + 2 methylmagnesium bromide.

In an attempt to isolate any intermediate compounds, bromoacetyl bromide was reacted with one and two moles of methylmagnesium bromide. In these reactions the bromoacetyl bromide was kept in excess by adding the Grignard reagent to it.

In a 2-liter, three-neck, round bottom flask, fitted with a stirrer, a reflux condenser and a dropping funnel was placed 101 gms. (5 moles) of bromoacetyl bromide in 250 cc. of anhydrous ether. The stirrer was started, and .5 mole of methylmagnesium bromide was added drop by drop. The reaction mixture separated into layers in the final stages of addition. The contents of the flask were hydrolyzed with ice and hydrochloric acid, extracted with ether, and dried over anhydrous sodium sulfate.

Upon fractionation under reduced pressure (13 mm.) no constant boiling fraction could be obtained. In the course of distillation, the contents of the distilling flask became black and viscous, until no further distillate would come over. If this viscous material were allowed to stand at room temperature, it finally solidified into a black, brittle substance. The distillate which came over clear, darkened upon standing. Some of the distillate came over in the range of bromoacetone (38-45° at 13 mm.), which was expected to be the intermediate. Attempts to prepare the semi-carbozone were unsuccessful (23). Further attempts to identify any fraction of the distillate were unsuccessful.

In the reaction of bromoacetyl bromide with two moles of methylmagnesium bromide, the results were the same as those above. No intermediate compound was isolated.

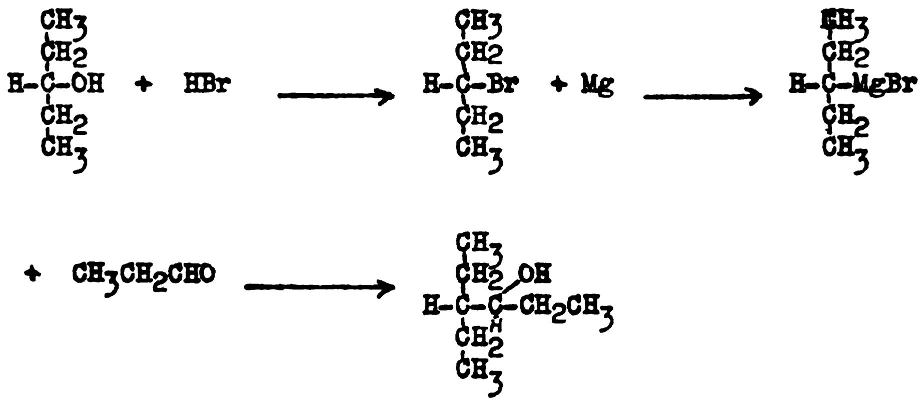
Reaction of bromoacetone with 2 moles of methylmagnesium iodide and with 4 moles of methylmagnesium bromide.

The procedure for both of these reactions is the same as that described for chloroacetyl chloride and methylmagnesium iodide. Bromoacetone in anhydrous ether was added to the Grignard reagent. The reaction mixture was set on the steam bath for 25 hours and was then hydrolyzed. The product obtained from both of these reactions was methylisopropyl carbinol.

Proof of Structure

Methylisopropyl carbinol was identified by means of derivatives. 3,5 Dinitrobenzoates and alpha-napthyl urathans were prepared from the product of the reaction of chloroacetyl chloride + 3.5 moles of methylmagnesium iodide, and from known methylisopropyl alcohol. The melting points of the derivatives were the same, and mixed melting points were found to melt the same (Constant given in Table of Results). The derivatives were prepared by the general method of preparing alcohol derivatives (24). No difficulty was encountered in their preparation.

The proof of structure of 4-ethyl-hexanol-3, which was the product of the reaction of chloroacetyl chloride with 3.5 moles of ethylmagnesium bromide, was established by synthesis. It may be shown as follows:



The bromide was made by refluxing for two hours diethyl carbinol with an excess (3 : 1) of 48% HBr. The bromide boiled at 114-117°. This was reacted with magnesium (as in the general method preparing Grignard reagents) for the Grignard reagent. To the Grignard reagent was then added propionaldehyde in anhydrous ether. The aldehyde was prepared by oxidising propyl alcohol (25). The reaction mixture was hydrolyzed with ice and hydrochloric acid, dried over sodium sulfate and fractionated under reduced pressure. The alcohol distilled at 42-45°/4, 162-65°/745.

Other constants were found to be as follows: Sp. Gr. 32/32 = .8365; n_D^{28} = 1.4287; γ^{32} 25.20 dynes/cm.^{2}

Efforts to prepare derivatives of this alcohol and of the alcohol obtained by the reaction of chloroacetyl chloride with ethylmagnesium bromide were unsuccessful. Therefore, physical constants were used to show that both alcohols were 4-ethyl-hexanol-3. The boiling point of the tertiary alcohol, diethyl-n-propyl carbinol (which would be the product if the reaction went as expected) is 155-159°. This is about 5° lower than the alcohol obtained.

TABLE OF RESULTS

Reactant	Grignard	Product	Boiling Point	Yield	Derivatives - M.P.	
					3,5 dinitro benzoate	alpha napthyl urathane
Chloroacetyl chloride	Methylmagnesium iodide	Methylisopropyl carbinol	109-110.5	48%	73-74	111-111.5
Chloroacetyl chloride	Methylmagnesium bromide	Methylisopropyl carbinol	109-110.5	51%	74.5	
Chloroacetyl chloride	Ethylmagnesium bromide	4-ethyl-hexanol-3	43-45/4 163-5/745	61% 45%		
Bromoacetyl bromide	Methylmagnesium iodide	Methylisopropyl carbinol	109-111.5	16%	74-75	112
Bromoacetyl bromide	Methylmagnesium bromide	Methylisopropyl carbinol	106-111	20%	73-74	
Bromoacetyl bromide	Ethylmagnesium bromide	4-ethyl-hexanol-3	40-43.5/4	5%		
Ethyl ester of chloroacetic acid	Methylmagnesium bromide	Methylisopropyl carbinol	108-112	24%	74	
Bromoacetone	2 m. of methylmagnesium iodide	Methylisopropyl carbinol	109-113	12%	72-73	
Bromoacetone	4 m. of methylmagnesium bromide	Methylisopropyl carbinol	109-112	18%	73-74	

Constants found for 4-ethyl-hexanol-3: B.P., 43-45°/4, 163-65°/745; Sp. Gr. 32/32 .8372; n_D^{28} 1.4291

γ^{32} = 25.32 dynes/cm.^{2}

SUMMARY

1. The reaction of alpha-halogen acid halides with Grignard reagents was studied.

2. A reaction mechanism was proposed.

3. Bromoacetone was established as one of the intermediate compounds.

4. The product of the reaction of chloroacetyl chloride and bromoacetyl bromide with methylmagnesium bromide and iodide was found to be methylisopropyl carbinol.

5. The product of the reaction of chloroacetyl chloride and bromoacetyl bromide with ethylmagnesium bromide was found to be 4-ethyl-hexanol-3.

6. Constants of 4-ethyl-hexanol-3 were determined as follows:

   B. P., 43-45°/4, 163-65°/745; Sp. Gr. 32/32 .8372; n_D^{28} 1.4291;
   γ^{32}= 25.32 dynes/cm.^{2}

BIBLIOGRAPHY

(1) Späth, Monatsh, 34, 1965, 1913, British Chem. Abst. 106, 1, 1914.

(2) Houben, Ber., 36, 3083, 1903.

(3) Gomberg and Cone, Ber., 39, 1461, 2975, 1906.

(4) Trotman, J.S.C., 127, 88, 1925.

(5) Carothers and Berchet, J.A.C.S., 55, 2813, 1933.

(6) Mitchovitz, Compt. rend. 200, 1601, 1935.

(7) Gilman and Fothergill, Rec. trav. chim., 48, 748, 1929.

(8) Gilman and Mayhue, Rec. trav. chim., 51, 47, 1932.

(9) Fisher, J.A.C.S., 52, 5038, 1930

(10) Kohler and Tishler, J.A.C.S., 54, 1594, 1932

(11) Aston, J.A.C.S., 57, 1920, 1935

(12) Winogradow, W., Ann. 191, 125, 1878.

(13) Gilman and Fothergill, J.A.C.S., 51, 3501, 1929.

(14) Bhagvat and Sudborough, C.A., 14, 1674, 1920

(15) Gilman and Heck, J.A.C.S., 52, 4949, 1930

(16) Hughes, Watson and Yates, J.C.S., 3318, 1931

(17) Grignard and Blanchon, C.A., 24, 1342, 1930

(18) Giovanni and Racciu, C.A., 27, 5719

(19) Anderson and Backmann, Lab. Man. of Org. Chem., p. 11, 1933

(20) Ward, J.C.S., 121, 1161, 1922, p

(21) Clarke, Org. Synth., Vol. 10, p. 12

(22)Clarke, Org. Synth., Vol. 10, p. 32

(23) Hoogeveen and Jansen, Rec. Trav. Chim., 51, 260, 1932

(24) Shriner and Fuson, Ident. of Org. Comp., Wiley & Sons, N. Y., p. 138

(25) Whitemore, Org. Synth. Vol. 12, p. 65