METALLIC BROMIDES AS CATALYSTS FOR THE FRIEDEL-CRAFTS KETONE SYNTHESIS

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INTRODUCTION

Since 1877 when Friedel and Crafts (19,20) discovered the reaction which bears their names, many fruitful researches in this field of Organic Chemistry have been accomplished. This important discovery became one stepping-stone of organic syntheses, and paved the way for the investment of tremendous amounts of capital.

Originally aluminum chloride was used as the condensing agent for the syntheses of the several possible types of organic compounds. However, further researches have proved that other metallic halides can be used for the same purpose, even though they are found to be less effective than aluminum chloride in some types of syntheses. (1), (13), (22), (55).

The main object of this work is to study the order of effectiveness of some of the metallic bromides as catalysts in the Friedel and Crafts ketone synthesis.

HISTORICAL

I. Theoretical:

Since the discovery of aluminum chloride as the condensing agent in the Friedel and Crafts reaction, various investigators have centered their interest on the metallic chlorides as catalysts in the various types of organic syntheses. This is probably due to the fact that they are cheap and easy to prepare and to handle. On the other hand there has been little said about the metallic bromides as catalysts. However, there are a few researches in which they have been used in organic condensations.

Staudinger and Bruson (50) used aluminum bromide, zinc bromide, tin bromide, antimony bromide, and ferric bromide as catalysts for the polymerization of cyclopentadiene.

Zelinskii and Turova-Pollock (58) found that cyclohexane rearranges into methylcyclopentane and dimethylcyclobutane under the influence of aluminum bromide.

Wertyporoch and Sagel (55) reported that a mixture of aluminum bromide and benzene, when subjected to slow reaction with the oxygen of the air, yields a dihydroxybenzene.

Wibaut, Diekmann and Rutgers (56) reported that gaseous hydrochloric acid and hydrobromic acid could be added to ethylene and propylene under the influence of bismuth tribromide or antimony tribromide.

Miukhailenko and Protosova (36) obtained a theoretical yield in the synthesis of dibenzyl when benzyl chloride was boiled in ethyl alcohol in the presence of a mixture of 0.4 mol ferric bromide to one atom of magnesium as catalyst.

Hofman and Wulf (28) used boron trifluoride in effecting condensation reactions such as the union of hydrocarbons with organic halogen compounds.

Calloway (14) found that organic fluorides such as the acyl and alkyl fluorides yield ketones and hydrocarbons respectively, when reacted with benzene in the presence of aluminum chloride as catalyst. He also found that zinc fluoride could be used as a condensing agent in the ketone synthesis, while aluminum fluoride has no effect on the same reaction.

Simons and Archer (48) used hydrogen fluoride as condensing agent between either olefins and benzene or alkyl halides and benzene and also in the alkylation of aromatic compounds with aliphatic halides. The reaction is carried out in liquid phase at 0° C and 760 mm. pressure. They found that the tertiary halides are the most reactive.

Pajeau (39) reported that beryllium dibromide cannot be used as a catalyst in the Friedel and Crafts ketone synthesis.

Holleman, Polak and Bewer (29) had used ferric bromide as a catalyst in the Friedel and Crafts ketone synthesis.

II. Analytical Method:

As to the quantitative determination of ketones, there are several methods described in the literature. Since most of them are inapplicable in one way or another, I need only to mention them as a matter of historical interest.

The colorimetric method described by Nikitin (37) and the gasometric one by Strache (52) cannot be used in this work because they are too inaccurate and require long time to perform the analyses.

Gravimetric

By far the commonest method of measuring yields of organic reactions is to isolate, purify and weigh the desired product. This procedure has been used to determine ketones formed in the Friedel and Crafts reaction by most investigators, including Gallay and Whitby (21), Riddell and Koller (42, 43), Groggins (23), and Gilman and Turck (22). However, as Wilson (57) pointed out, this method is very inaccurate on small amounts, and larger runs are impossible in our work on account of the cost of catalyst.

It is also possible to isolate a derivative of the product. Ketone mono- and dinitrophenylhydrazones have been found insoluble enough to permit their use in determining the ketones, (32), (24), but in our work the presence of toluene prevents the precipitation of these compounds.

Volumetric

Olivier (38) measured the amount of unreacted benzoyl chloride to determine the amount of reaction when benzoyl chloride was treated with benzene in the presence of catalyst. The residual benzoyl chloride was hydrolyzed and the benzoic acid extracted and titrated with alkali. The obvious disadvantage of this method is that it sets up an abnormal condition in employing excess halide instead of excess of benzene.

Martin, Pizzolato, and McWaters (35) studied the kinetics of the Friedel and Crafts reaction of benzoyl chloride with toluene and used the amount of hydrogen chloride evolved as a measure of the extent of reaction, but this is not always true because as long as the reaction mixture is refluxed, there

is an evolution of hydrochloric acid gas (45), (24), (14). Nevertheless, the same method has been used by Steele (51), Ulich and Heyne (53), Clement and Savard (15), Chopin (16), and Boswell and McLaughlin (10).

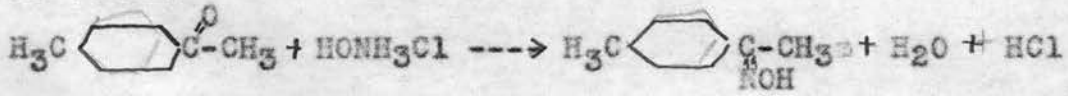
Lautenschlaeger (34) used an iodometric method for the determination of ketone with an excess of hydrazine sulfate. The excess of hydrazine was found by adding an excess of iodine and titrating the excess with sodium sulfite. (2), (4)

Romeo and D'Amico (44) determined aldehydes and ketones by the formation of neutral addition products of aldehydes or ketones with sodium sulfite and potassium bisulfite. The excess acidity after the reaction is titrated with 0.5 N sodium hydroxide and the amount of bisulfite reacting with the ketones or aldehydes is measured by difference.

Methyl ketones have been determined quantitatively by heating them with alkali and excess of iodine which converts them into iodoform and then titrating the excess iodine with sodium thiosulfate (31), (30), (17), (26), (3).

The hydroxylamine hydrochloride method of Bryant and Smith (12) was used in this work. It is preferred because it requires less time to perform the analyses. It is more accurate and less expensive than the other methods and there is no need of isolating the product. It is an acidimetric method for determination of ketones and aldehydes using hydroxylamine hydrochloride. The hydrochloric acid liberated is a measure of the ketone or aldehyde present.

Reaction:



The method can be applied to carbonyl compounds of aliphatic, alicyclic and aromatic structure. The method was used by Brochet and Cambier (11) and modified by Bennett and Donovan (7). In the method the hydroxylamine base was liberated from the hydrochloride by the addition of alcoholic sodium hydroxide and then allowed to react with the carbonyl compound. The unused hydroxylamine is determined alkalimetrically. (6), (8), (40), (41), (47), (46), (54).

EXPERIMENTAL

I. Synthesis:

a. Catalysts:

The catalysts used in this work were all anhydrous: aluminum bromide, antimony tribromide, ferric bromide, tellurium tetrabromide, tin tetrabromide, titanium tetrabromide, and zinc bromide.

The anhydrous aluminum bromide was prepared as directed by Kablufoff (33) with modification of equipment and procedure. A 250 ml. Erlenmeyer flask containing about 100 ml. of liquid bromine is connected to a bubble counter containing concentrated sulfuric acid leading to a combustion tube containing dried aluminum metal, heated with an electric furnace. The other end of the tube is slightly bent to fit a 125 ml. distilling flask as a receiver, which is connected to a suction flask containing sodium hydroxide solution. The suction flask is also connected to a water pump. Before the bromine vapor is passed through the reaction chamber, the aluminum metal is first heated to dull redness. Then the bromine is warmed up gently and the dried vapor is passed over the red hot metal by means of a controlled water suction pump. The reaction product is purified by repeated fractional distillation. The fraction coming out at 266-270° C was collected. (Literature gives 268° C as the true boiling point.)

The same method was applied in the preparation of ferric bromide, tellurium tetrabromide and bismuth tribromide, except that ferric bromide was purified by resublimations. In the case of the preparation of bismuth tribromide the yield was extremely poor, so that it was abandoned as a catalyst

in this work.

The anhydrous antimony tribromide was prepared as directed by Serullos (49). The powdered dry antimony was introduced in small portions into a retort containing liquid bromine, agitating the retort after each admixture. When the combustion had ceased, the bromide was distilled from the excess of antimony. It was purified by fractional distillation. Observed boiling point 280-282° C. (Lit. 280° C b.p.)

Anhydrous stannic tetrabromide was prepared as directed by Baumer and Krepelka (5). Liquid bromine was allowed to drip slowly through a dropping funnel into a 250 ml. distilling flask containing 25 g. of dry powdered tin. When the reaction ceased the product was purified by repeated fractional distillation. Observed boiling point 200-203° C. (Lit. 202° C b.p.)

Anhydrous titanium tetrabromide was prepared as directed by Bond and Crane (9). Gaseous hydrobromic acid was allowed to bubble through titanium tetrachloride held at 50° C. After hydrobromic acid had passed for a period of 24 hours, the reaction mixture was allowed to cool. The product was purified by fractional distillation six times. Observed boiling point, 230-233° C. (Lit. 230° C b.p.)

Anhydrous zinc bromide was prepared by heating a commercial grade zinc bromide in an inverted y-tube with both legs sealed. The catalyst was distilled from one leg into the other leg of the tube under reduced pressure.

In view of the fact that the metallic bromides are even more hygroscopic than the corresponding chlorides, it was

necessary during the course of their preparation to keep them away from moisture as much as possible. After they were prepared, they were kept in a desiccator until ready to be used.

b. Chemicals used

Friedel and Crafts reagents:

The acetyl chloride used was C. P. grade. In order to lessen contaminating it with moisture, portions were put into eight one-ounce glass stoppered bottles and sealed in with sealing wax. One was opened at a time as needed.

The toluene used was C. P. grade. However, it was dried with calcium chloride and redistilled twice.

Analytical reagents:

The reagents were prepared as directed by Bryant and Smith (12). The hydroxylamine hydrochloride used was C. P. grade. The 0.5 N solution was made by dissolving 35 gm. of C. P. hydroxylamine hydrochloride in 160 ml. of distilled water and diluting to one liter with 95% ethanol.

The indicator used was bromophenol blue. It is made by dissolving 0,5 gram of bromophenol blue in 100 ml. of 95% ethanol. The pyridine was ommitted in this case because certain details of the analytical procedure were modified as will be described later.

The standardized 0.5 N solution of sodium hydroxide was made by dissolving 20 grams of C. P. sodium hydroxide in one liter of 90% methanol. This alcoholic base was used to titrate the hydrochloric acid liberated in the reaction between the p-methylacetophenone and the hydroxylamine hydrochloride. The sodium hydroxide solution was twice restandardized against

standard hydrochloric acid during the course of this work. This was done to be sure that there was no fluctuation in the normality.

The p-methylacetophenone which was used in the preliminary analyses was students' preparation. It was purified twice by fractional distillation.

c. Procedure:

In order to determine the true effectiveness of the catalysts in the Friedel and Crafts ketone synthesis all experimental conditions were kept constant except that the catalysts were varied. In this work the procedure as directed by Wilson (57) was followed, except that some modifications have been made in the nature of improvement of equipment and of analytical method. Since the yields were based on the weight of the acetyl chloride, it was necessary to calibrate the pipette used, which was found to deliver 1.0811g. of that chloride.

Before doing any synthesis several analyses were made using pure p-methylacetophenone as known samples. The main purpose of this was to get familiar with the end point of the titrations which would be met in the later analyses.

In performing the Friedel and Crafts ketone synthesis, the following procedure was carried out. Six ml. of toluene were pipetted into a dry 200 ml. flask, specially made for this work. Then 0.014 mol of the catalyst was weighed in a rubber stoppered vial. The weighing must be done as quickly as possible and the container be kept stoppered all the time, except when adjusting the desired weight of the catalyst. After weighing the catalyst the flask was put over a water

bath and 1.081 g. of acetyl chloride added. Then the catalyst was immediately added, and the flask attached to the dry reflux condenser. The reaction mixture was heated for one hour at the boiling point of water. Then a small amount of distilled water was added through the condenser, to hydrolyze the catalyst and the molecular compound with the ketone produced. The flask was detached from the condenser. Then the reaction mixture was made neutral by the addition of 10% sodium hydroxide, using phenolphthalein as an indicator. Again the flask was attached by ground glass connections to a condenser arranged for distillation. Then 75 ml. of the total volume was distilled into a 100 ml. separatory funnel. In order to reduce bumping and the danger of splashing over the colloidal hydroxide of the metal, clay chips were added. The distillation was carried out slowly and with great care.

After the distillation, the condenser was rinsed with 3 ml. of toluene and drained into the separatory funnel. The toluene layer was separated from the water layer. To be sure that all the dissolved product was removed from the water layer it was necessary to make repeated extractions. This was done by adding a little salt (NaCl) and 2 ml. of toluene to the water layer, shaking well and separating the toluene layer. This was done 3 times. Before putting the product into the pressure bottles, it was tested for neutrality and adjusted to that point if necessary. After all these steps had been finished, the final product was ready for quantitative determinations.

Analysis

The Iodoform Method: It was first intended to use the iodoform method for the estimation of acetophenone, as described by Haughton. In this method acetone was determined by treating with excess sodium hydroxide and standard iodine solution, acidifying to regenerate unchanged iodine, and titrating it with standard sodium thiosulfate solution. The difference between a blank and an actual run measures the amount of iodine reacting, and thus the amount of methyl ketone.

To test this method runs were made with known samples of p-methylacetophenone. This ketone was chosen because it was also the one formed in the Friedel and Crafts synthesis studied. At first recoveries of 65-85% of the ketone were obtained. In an attempt to increase this yield, the reaction mixtures were shaken mechanically for two hours before acidifying them, but the results were still low and inconsistent. It was then supposed that failure of the method is due to the slight solubility of the ketone in aqueous sodium hydroxide; accordingly, a solution of sodium hydroxide in methanol was employed. This time the results indicated that 95-150% of the ketone reacted. To find the cause of this abnormal behavior, duplicate knowns were run at 5°, 25°, and 50° C; but the yields were still too high and variable. Since the method apparently could not be depended upon, it was abandoned in favor of the hydroxylamine method.

Hydroxylamine method: The original procedure described by Bryant and Smith (12) was modified because in it the end point of the titration is exceedingly indistinct. Instead of

heating the mixture of sample, hydroxylamine hydrochloride and indicator together I left out the indicator until the titration was to be done. Preliminary analyses showed that the two methods gave practically the same results, but that the end point in the modified method is more easily seen. In analysing the product, two samples were always run at the same time.

20 ml. of hydroxylamine hydrochloride were pipetted into each of the pressure bottles containing ketone samples. The bottles were capped tightly and each rubber gasket was wetted with a drop of water in order to permit it to slide into place tightly. The bottles were put in the oven (having a temperature of 120° C) for two hours. Simultaneously three blanks containing toluene and hydroxylamine hydrochloride were also heated for the same period of time. These blanks were used for color comparison.

After the required time had elapsed, the samples and blanks were allowed to cool. Then the blanks were first titrated with the standard 0.5 N sodium hydroxide, using bromophenol blue as indicator. The amount of base required for each of the blanks was recorded on that bottle. This furnished three shades of color in the neighborhood of the end point. Then the samples were each titrated to all the three colors, and the titration which gave the most intense green color was taken as the end point.

On the preliminary analyses of known weights of pure p-methylacetophenone, the amount of ketone reacting with the hydroxylamine hydrochloride was found to be on the average,

99.3%. A correction factor was determined by heating one gram of pure p-methylacetophenone for one hour, steam distilling and analysing. It was found that the results in the duplicate runs gave an average value of 95.8% of the original sample accounted for. In order to obtain the actual ketone content of the sample, each apparent weight of the unknown ketone found was therefore divided by the correction factor 0.958.

RESULTS AND DISCUSSION

In order to compare the activity of two halides of the same metal when used as catalysts in the ketone synthesis, Table I was constructed to show the yields.

TABLE I

Yields of p-Methylacetophenone

Metallic Chloride Catalysts			Metallic Bromide Catalysts	
Catalysts		Yields	Catalysts	Yields
1. $AlCl_3$	(57)	1. 54.8% 2. 55.5%	1. $AlBr_3$	1. 70.7% 2. 70.4%
2. $FeCl_3$	(57)	1. 40.5% 2. 39.7%	2. $TiBr_4$	1. 10.4% 2. 11.2%
3. $SnCl_4$	(57)	1. 27.7% 2. 27.5%	3. $SbBr_3$	1. 6.7% 2. 6.3%
4. $TeCl_4$	(57)	1. 19.2% 2. 18.8%	4. $FeBr_3$	1. 5.6% 2. 5.2%
5. $TiCl_4$	(57)	1. 15.1% 2. 15.2%	5. $ZnBr_2$	1. 4.1% 2. 3.9%
6. $ZnCl_2$	(57)	1. 7.23% 2. 7.4%	6. $TeBr_4$	1. 1.6% 2. 1.4%
7. $SbCl_5$	(57)	1. 0.91% 2. 1.21%	7. $SnBr_4$	1. 0.9% 2. 0.9%
8. $SbCl_3$	(18)	none		

TABLE II

Distribution of Effective Catalysts in the Periodic Table

Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Li	Be	B	C	N	O	F	
Na	Mg	$AlBr_3$	Si	P	S	Cl	
K	Ca	Sc	$TiBr_4$	V	Cr	Mn	$FeBr_3$ Co Ni
Cu	$ZnBr_2$	Ga	Ge	As	Se	Br	
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru Rh Pd
Ag	Cd	In	$SnBr_4$	$SbBr_3$	$TeBr_4$	I	
Cs	Ba	La	Ce				
			Hf	Ta	W	Re	Os Ir Pt
Au	Hg	Tl	Pb	Bi	Po	Ab	
Vi	Ra	Ae	Th	UX_2	U		

Table II shows the location on the periodic table of the elements yielding the active catalysts used.

Judging by the yields given by two different halides of the same types of synthesis under the same conditions, the metallic chlorides are more effective as catalysts than the corresponding bromides with the exception of aluminum bromide and antimony tribromide.

Therefore, their order of activity in the ketone synthesis would be: $AlBr_3 > AlCl_3$; $FeCl_3 > FeBr_3$; $SnCl_4 > SnBr_4$; $TeCl_4 > TeBr_4$; $TiCl_4 > TiBr_4$; $ZnCl_2 > ZnBr_2$; $SbBr_3 > SbCl_5$. So far as can be found in the literature, this is the first time the metallic bromides have been reported as catalysts in the Friedel and Crafts ketone synthesis, except aluminum bromide and ferric bromide, even though aluminum bromide, ferric bromide, antimony tribromide, stannic tetrabromide and zinc bromide had been reported as catalysts in the polymerization of hydrocarbons.

In connection with this work, I found that the elements yielding catalysts which gave yields in the ketone synthesis conform to a previous generalization of Calloway (13) about their characteristics.

1. All those tested have variable valence except aluminum and zinc.
2. They are mostly located in the central part of the periodic table.
3. The catalysts have fairly high boiling points.

SUMMARY

1. The anhydrous bromides of aluminum, titanium (ic), antimony (ous), iron (ic), zinc, tellurium (ic), and tin (ic), have been prepared and tested as catalysts for the Friedel and Crafts synthesis of p-methylacetophenone from acetyl chloride and toluene.

2. This ketone is best determined by the hydroxylamine method. Attempts to use the iodoform method gave highly erratic results under varying conditions.

3. Aluminum bromide is better than any other bromide or chloride yet studied as a catalyst for this synthesis. With the additional exception of antimony tribromide, the metallic bromides are poorer catalysts than the corresponding chlorides. Among the bromides the order of activity is: $AlBr_3 > TiBr_4 > SbBr_3 > FeBr_3 > ZnBr_2 > TeBr_4 > SnBr_4$

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BIOGRAPHY

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