

QUANTITATIVE COMPARISONS OF METALLIC
CHLORIDE CATALYSTS IN THE FRIEDEL-CRAFTS KETONE
SYNTHESIS

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By

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Bachelor of Science

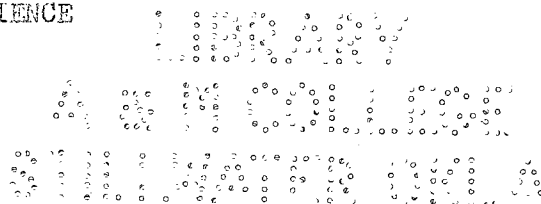
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INTRODUCTION

This is a continuation of the work dealing with the study of catalysts for the Friedel-Crafts ketone synthesis started by Wilson (40), and continued by Suguitan (37), and Johnson (19). The results found by Wilson and Johnson with regard to optimum ratio of metallic chloride catalyst to a given amount of acetyl chloride were used as a basis for this work. The principal variation made here was the employment of lower and more nearly constant temperatures and the consistent use of the Perrier (31) or reverse order of addition of reagents. All reactions were carried out at room temperatures, 20-25°C, and the variation of yield with time of reaction was determined.

No attempt will be made here to define a mechanism for the reaction but it is hoped that the additional data found may some day be used for this purpose.

Because the Friedel-Crafts reaction finds, perhaps, greater industrial application than any other single type of reaction (4, 16), a knowledge of the true mechanism would be of far reaching importance.

HISTORICAL

Friedel and Crafts (12), the discoverers of the reaction that has come to bear their name, learned early in their researches that the active condensing agent in the reaction was aluminum chloride (4). Because of the versatile nature of the reaction and consequently its extreme importance in organic synthesis, rather extensive investigations have been carried out by many workers. The chlorides of metals other than aluminum have been found to act as catalysts, the important ones being zinc chloride, ferric chloride, and stannic chloride (4, 23). In fact, these three have been found to be more effective than aluminum chloride in certain specific reactions (2, 5, 11, 25, 39). The latter, however, is still the catalyst most generally employed especially in the ketone synthesis. Calloway presents an excellent review of the subject (4).

Besides those mentioned above, other metallic chlorides which have been studied and are known to be catalysts are antimony trichloride (9, 29), antimony pentachloride (9), beryllium chloride (3), bismuth trichloride (40), gallium trichloride (38), molybdenum pentachloride (21), platonic chloride (26), tellurium dichloride, tellurium tetrachloride (40), thallium trichloride (20), tungsten hexachloride (21), uranium tetrachloride (19, 21, 24), and uranium trichloride (19).

Wilson (40) tested some twenty-four metallic chlorides and Johnson (19) two, which would not function as catalysts. These chlorides found to be inactive by other workers also are: calcium chloride (4), chromic chloride (8, 14), cuprous chloride (14), lead dichloride and silicon tetrachloride (4). Johnson (19) was not able to decide definitely

whether PbCl_4 was a catalyst or not. Calloway (6) reported it as a non-catalyst.

Studies have been made on the rate of the reaction for both the ketone and the hydrocarbon synthesis (27, 33) and a comparison of the efficiency of various catalysts would really be a comparison of the rates were it not for the fact that consecutive and side reactions complicate the Friedel-Crafts reaction. Calloway (4) and others give the order for decreasing activity of Friedel-Crafts catalysts as: aluminum chloride, ferric chloride, zinc chloride, stannic chloride, titanium tetrachloride, and zirconium tetrachloride.

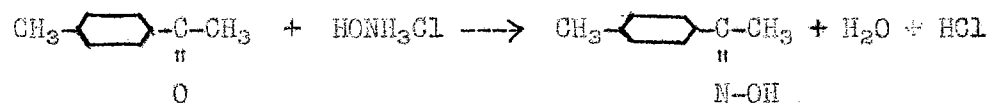
Some quantitative comparisons other than those of Wilson (40) and Johnson (19) have been made but only with mixed catalysts (13, 15, 16, 33).

At present the only practical basis of comparison is by measuring the extent of the reaction by determining the amount of yield as was done in this work. Acetyl chloride and toluene react in the presence of some metallic chlorides to produce the ketone p-methylacetophenone. Keeping all variables other than time of reaction constant, the extent of the reaction as catalyzed by various metallic chlorides was determined. The optimum ratio of moles of catalyst to moles of acetyl chloride as found by Johnson (19) was used in every run for which data were available.

The hydroxylamine hydrochloride method of measuring yield found by Wilson (40) to be the most accurate without being too laborious, and also used successfully by Johnson (19), was chosen. As others (15, 16, 33) have pointed out, the actual isolation of the ketone is not only impractical but also inaccurate when used in small scale runs. Wilson (40) has pointed out also that the volume of hydrogen chloride evolved (7, 13, 27)

need not be a measure of the extent of the reaction, as it is liberated merely by refluxing together aluminum chloride and acetophenone (7, 18, 35). Other possible methods of determining the extent of the reaction, are, in general, too troublesome to be used.

The hydroxylamine hydrochloride method (1) consists in titrating the hydrochloric acid liberated in the following reaction,



with a standard sodium methoxide solution, the quantity of sodium methoxide used giving directly the quantity of ketone formed. The modification as used by Johnson (19), that is, the use of absolute methanol in place of 95 per cent ethanol as reaction medium, to get a sharper end point, was used.

EXPERIMENTAL

Substances Used

Catalysts

C. P. anhydrous, iron-free, aluminum chloride was purchased from Mallinckrodt Chemical Company.

C. P. anhydrous ferric chloride was obtained from Eimer and Amend.

C. P. antimony pentachloride was redistilled just before use to remove any decomposition products.

The stannic chloride was used C. P. grade.

C. P. bismuth trichloride was distilled before using.

The titanium tetrachloride was also redistilled before using.

Anhydrous molybdenum pentachloride was prepared in the following manner: Powdered molybdenum metal was placed in a combustion tube which could be heated by means of an electric furnace. Chlorine gas was passed through concentrated sulfuric acid to assure its being dry, and passed through the tube, over the metal, for about thirty minutes. After this time, all air and water vapor had been swept out and the furnace, controlled by means of a rheostat, was turned on. Reaction began to take place at about 200°C. The temperature was gradually raised to 300°C in order that the pentachloride formed would sublime in the tube just beyond the end of the furnace. The excess chlorine was absorbed by means of sodium hydroxide solution. The product, after cooling in a stream of chlorine, was quickly plunged into small glass-stoppered bottles and immediately placed in a vacuum desiccator. No further purification was deemed necessary, even though chlorine was probably adsorbed on the surface.

Anhydrous columbium pentachloride was prepared in exactly the same

way as molybdenum pentachloride.

Anhydrous selenium tetrachloride was prepared in a manner analogous to that used in the preparation of molybdenum pentachloride with the exception that not so high a temperature was required (200-250°C).

Anhydrous tellurium tetrachloride was made by passing dry chlorine into a distilling flask containing the free metal (28). Once started by heating gently, the reaction is highly exothermic. The product was purified by distillation.

Anhydrous tellurium dichloride was prepared by refluxing tellurium tetrachloride with a slight excess of tellurium metal (34). The product was purified by distillation.

C. P. beryllium chloride was purchased from the City Chemical Company.

Anhydrous zinc chloride was obtained by fusing C. P. zinc chloride in a small crucible, and while still liquid was poured into a dry mortar where it was allowed to cool slightly and then rapidly ground to a fine powder.

Friedel-Crafts Reagents

Merck's reagent grade toluene was used without further purification. C. P. acetyl chloride was put into small glass-stoppered bottles and stored in a desiccator. Every precaution was taken to prevent its hydrolysis.

Analytical Reagents

The hydroxylamine hydrochloride solution was prepared in a manner identical to that which Johnson (19) used. Thirty-five to forty grams of C. P. hydroxylamine hydrochloride was dissolved in a small amount of absolute methyl alcohol and then diluted to 1000 ml with the same solvent.

This gives approximately 0.5 normal solution.

The butter yellow used as the indicator was prepared by dissolving recrystallized p-dimethylaminoazobenzene in absolute alcohol.

By dissolving the calculated amount of sodium in absolute methanol an approximately 0.1 normal solution of sodium methoxide was prepared.

It was standardized against potassium acid phthalate.

PROCEDURE

The aromatic compound used was toluene. This choice was made because toluene is relatively inexpensive, easy to obtain and keep in very pure form, and is about average in its degree of activity. It is not so active as anisole, which gives good yields of ketone in the absence of a catalyst, nor quite as slow to react as benzene. It is desirable to use a compound which will give a large yield to minimize the percentage of error.

A standard procedure was used in making every run, as follows: A 250 ml, round-bottom, long-neck flask equipped with a ground glass joint was used as the reaction vessel. Into the flask, previously dried for at least six hours in an oven at 110°C, was added 1 ml of acetyl chloride from a calibrated pipette; it delivered 1.089 grams. The catalyst was then added to the acid chloride. In the case of a liquid, the required amount was obtained by employing a graduated pipette; if the catalyst was a solid, it was rapidly weighed out to the nearest centigram on glazed paper and transferred immediately to the reaction flask.

The addition of metallic chlorides to acetyl chloride results in the formation of a molecular complex and is generally accompanied with the evolution of a considerable quantity of heat. In order that no acetyl chloride volatilize and be lost because of this heating effect, the reaction flask was kept in an ice bath until all reactants had been added.

After the catalyst had been added to the acetyl chloride, 10 ml of toluene was added by means of a pipette.

The quantity of catalyst to be used was obtained from the data

compiled by Johnson (19). That ratio of moles of catalyst/moles of acetyl chloride which gave the maximum yield in each individual case was used. The actual ratio for each run is given in Table I.

After all the reactants were added, the flask, provided with a glass-ground joint, was attached to a reflux condenser and allowed to stand at room temperature, 20-25°C, for the desired length of time. This reaction time varied in individual cases from one-quarter of an hour to twenty-four hours (one run of SnCl_4 , one hundred and fifty-six hours).

The use of a reflux condenser was really unnecessary as none of the reactions proceeded so vigorously to require it. It was necessary in previous work and retained here merely as a convenience.

After the reaction time which was chosen was complete, water was poured down the condenser, hydrolyzing the catalyst and thereby instantly stopping the reaction.

Potassium hydroxide solution was added to the hydrolyzed mixture until in excess as indicated by phenolphthalein. This neutralization process is necessary as any excess acid would later distil over along with the ketone and falsify the results, the analytical method employed being essentially an acidimetric titration.

After the reaction mixture was made alkaline, sufficient water was added to bring the total volume to about 150 ml. The flask was connected to a condenser with a ground-glass joint and the toluene and product steam-distilled. The connecting joint was so constructed that steam could be passed directly into the reaction mixture through glass tubing which passed through the joint by way of a ring seal down into the liquid.

Approximately 75 ml of distillate was collected in a separatory funnel. Just before the distillation was complete, the water was allowed to

drain from the condenser in order that the steam which would then pass through would sweep out any ketone which might adhere to the walls. Because steam was passed directly into the reaction flask and not generated there by applying heat to the mixture, no difficulties as regards bumping or frothing were encountered. Earlier workers had met with these difficulties (19, 40).

To the distillate in the separatory funnel approximately 15 g of sodium nitrate was added to salt out the product. The toluene-ketone layer was carefully separated and two more extractions were made using 5 ml portions of benzene to assure the complete removal of ketone. The accumulated extractions were brought together in a glass-stoppered bottle and to this solution was added 20 ml of an approximately 0.5 normal solution of hydroxylamine hydrochloride in absolute methyl alcohol. To assure accuracy the stock solution of hydroxylamine hydrochloride must be kept neutral. This is most easily accomplished by adding a small quantity of sodium methoxide whenever necessary.

After the above addition had been made, the ketone solution was allowed to stand for about twenty-four hours. The reaction between p-methylacetophenone and hydroxylamine hydrochloride is rather slow and does not go to completion spontaneously. The hydrochloric acid which is liberated in the reaction was titrated with standard sodium methoxide. Butter yellow was the indicator used. The first end point reached is not permanent and the titration was repeated at convenient intervals of about twenty-four hours. The permanent end point was light peach in color.

To test the validity of the analytical method, blanks, omitting the acetyl chloride, were occasionally run. Never was evidence found to throw

doubt upon the accuracy of the method.

The use of corks or rubber stoppers was avoided in order that none of the ketone formed or reactants used might be lost by absorption.

RESULTS

Table I

Variation of Yield with Reaction Time

Catalyst	Moles catalyst/ moles CH_3COCl	Time (Hours)	Yield (%)
AlCl_3	1.6	1/4	74.20, 73.20
		2	73.90, 73.20, 73.00
		2 1/2	73.30, 73.10
		3	73.00, 73.10
FeCl_3	1.2	1/4	70.50
		1	73.50
		2	72.00
		4	73.50
		6	72.20
CoCl_2	1.3	1 1/2	67.70
		3	74.10, 74.00
		4	71.70
		6	73.50
		9	73.50
SbCl_5	1.2	1	57.00
		3	60.40
		4	58.70
		6	59.00
		24	65.40

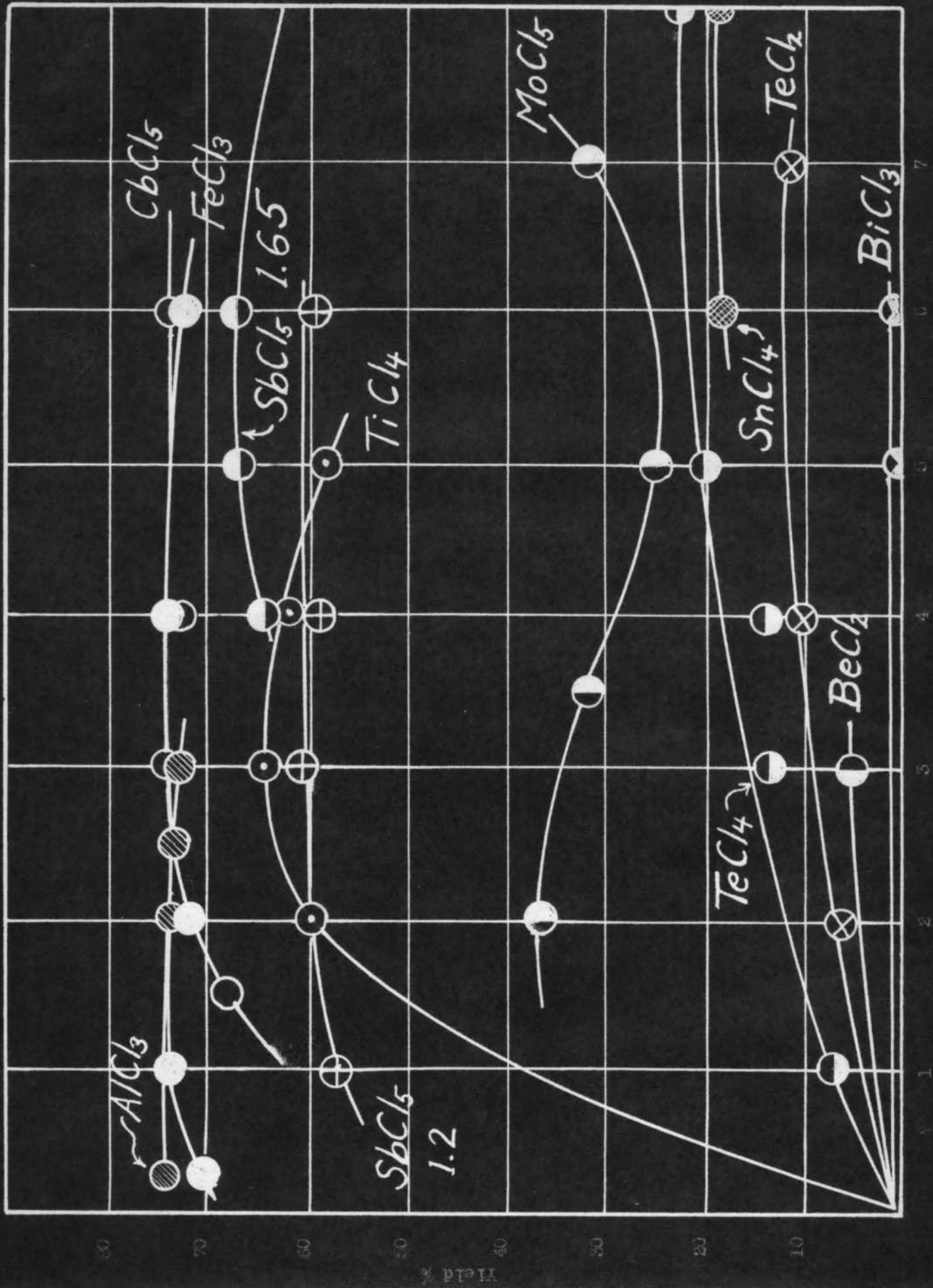
Table I
continued

Catalyst	Moles catalyst/ moles CH_3COCl	Time (Hours)	Yield (%)
SbCl_5	1.65	4	64.20
		5	66.50
		6	66.30
		9	58.80
TiCl_4	3.0	2	59.50
		3	63.10, 65.10
		4	61.40
		5	57.80
MoCl_5	1.2	2	56.70
		3 1/2	51.90
		5	25.50
		7	32.00
TeCl_4	1.0	1	7.20
		3	13.40
		4	13.70
		5	20.00
		8 1/2	23.80
		24	25.40
TeCl_2	1.8	2	6.68
		4	10.70
		7	11.40
		11	13.40
		24	15.30

Table I
continued

Catalyst	Moles catalyst/ moles CH_3COCl	Time (Hours)	Yield (%)
SnCl_4	2.0	6	19.10, 17.90, 16.50
		8	20.45, 19.20, 18.90, 16.90, 16.60, 16.50
		156	28.80, 28.40
BeCl_2	1.2	3	5.35
ZnCl_2	0.8	24	2.65
BiCl_3	1.0	5	0.55
		6	0.72

Selenium tetrachloride was found to give no ketone.



Reaction Time in Hours

Yield %

DISCUSSION OF RESULTS

A general deduction as to the advantages of using the Perrier method of reagent addition in the Friedel-Crafts ketone synthesis might be that in no case will it impair the yield and in most cases will increase it. This is to be accounted for, evidently, by the fact that the catalyst and acid chloride form a complex of the general formula $Al_2X_6 \cdot 2RCOCl$, at least in the case of aluminum compounds. Kohler (22) assigned this formula to the complex from freezing point and boiling point determinations. He also showed that the aluminum halide forms an addition compound with the ketone produced, the formula being $Al_2X_6 \cdot R_2CO$. His work was confirmed by Pfeiffer and Haack (32).

According to Olivier (30) these complexes hinder the reaction. It is our belief, however, that the preliminary formation of the acetyl chloride-catalyst complex must be an aid to the reaction as increased yields using the Perrier method has been reported by other investigators also. It has been shown by Groggins (16), however, that $AlCl_3$ is so closely bound to the carbonyl of the ketone (before hydrolysis) that it is not available for further synthesis. The formation of this complex, then, hinders the reaction if the metal halide is not in excess.

Acetyl chloride, being quite volatile, is easily lost unless special precautions are taken. In the Perrier method all of the acid chloride is combined in the non-volatile addition compound. As a result, it is not necessary to drip toluene down the reflux condenser to scrub acetyl chloride free from the escaping vapors of hydrogen chloride as had to be done in previous work.

Allowing the reaction to take place at room temperature is favorable, as evidenced by increased yield, for certain catalysts and

detrimental for others. Those catalysts which are capable of giving good yields when the reaction mixture is heated, give even larger yields when the reaction is allowed to take place at room temperature, assuming that the Perrier order of reagent addition is used in the latter case. Catalysts for which this holds true include AlCl_3 and FeCl_3 . Those metallic chlorides which were poor or only fair catalysts in previous work, are even lower in their catalytic activity when the reaction is allowed to take place at about 25°C . Here are included SnCl_4 , TeCl_2 , TeCl_4 , and BiCl_3 .

Titanium tetrachloride, however, was a definite exception to this last generalization. By its use the yield of ketone was increased proportionally more than that produced by any other metallic chloride by using the modifications employed in this research. The yield was improved from a maximum of 35 per cent as found by Dermer and Dermer (10) to 65 per cent.

Calloway (7) has shown that AlCl_3 will cause self-condensation of ketones:



It can be concluded by analogy that compounds which will catalyze ketone formation will also catalyze its condensation. A comparison of results would also seem to indicate that increased temperature greatly favors this condensation. The decrease in yield from 65 per cent to 35 per cent of the theoretical by allowing the reaction to take place at 80°C instead of at 25°C , using TiCl_4 as catalyst, can thus be explained. The rather slight, but nevertheless certain, increase in yield in the case of AlCl_3 and FeCl_3 , as compared with the results of earlier

workers, is to be explained in the same way.

Johnson (19) showed that with nearly all catalysts there was an eventual decrease in yield with increase in reaction time. In this work, however, only those runs using SbCl_5 in large excess and TiCl_4 as catalysts exhibited this falling-off of yield. As a matter of fact, in the cases of SbCl_5 where the ratio of moles of catalyst/moles of acetyl chloride was 1.2, TeCl_2 , and SnCl_4 , maximum yields were obtained only on allowing the reaction to stand for twenty-four hours for the first two and one hundred fifty-six hours for the last.

For elements which are capable of existing in more than one valence state, only the chloride in the higher valence state will show catalytic activity. The chlorides of antimony, uranium and tellurium are exceptions to this rule. In fact, UCl_3 is reported to be a better catalyst than UCl_4 (10) and Johnson (19) found TeCl_2 to give larger yields of ketone than did TeCl_4 . We have found, however, that the order of reactivity of the chlorides of tellurium is reversed under conditions used in this research and is in accordance with what one would expect from the study of other catalysts.

It was believed that an increase in the quantity of catalyst used might have the same effect as a prolonged reaction time, and results of experiments in which this was actually tried show that the reaction took place more rapidly but not to any greater extent. The optimum ratio of moles of SbCl_5 /moles of acid chloride of 1.2 as found by Johnson (19) gave the maximum yield only after allowing the reaction to take place for twenty-four hours. Using a ratio of moles of SbCl_5 /moles acid chloride of 1.65 the same maximum yield was obtained in five hours.

Columbium pentachloride was found to act as a catalyst in the

Friedel-Crafts hydrocarbon synthesis (17) but this is the first time that it has been reported as a catalyst in the ketone synthesis. It is as effective a catalyst as AlCl_3 but does not reach its maximum yield as rapidly. Since it forms a very thick, pasty reaction mixture, it was thought that this might hinder its catalytic activity. Two additional runs were made using a further excess of toluene but no variation in the amount of yield was observed.

The rather peculiar curve obtained when yield is plotted against time of reaction in the case of MoCl_5 cannot be explained at the present time. The variations in the yields, however, seem to be sufficiently great that they could not have been the result of experimental error. The points were not checked as no more of the catalyst was available.

Bredereck and his co-workers (5) report an 80 per cent yield of p-methylacetophenone using BeCl_2 as catalyst. They carried out the reaction at 35-40°C and used a ratio of moles of BeCl_2 /moles of acetyl chloride of 1.6. The poorness of yield we obtained in this research is probably due to the lower temperature used and also the smaller ratio of catalyst to acid chloride. Only one run was made with BeCl_2 as but a very limited supply of this catalyst was available.

Selenium tetrachloride is here reported as a non-catalyst for the first time.

Of the catalysts used in this research the order of decreasing efficiency is: AlCl_3 , SbCl_5 , TiCl_4 , MoCl_5 , SnCl_4 , TeCl_4 , TeCl_2 , BeCl_2 , ZnCl_2 , and BiCl_3 . This order is somewhat different from that which Johnson (19) found. He listed them in decreasing order of efficiency as follows: AlCl_3 , SbCl_5 , FeCl_3 , SnCl_4 , UCl_3 , TeCl_2 , TiCl_4 , TeCl_4 , BiCl_3 , UCl_4 , ZnCl_2 .

Wilson (40) showed that HgCl_2 would not catalyze the reaction between acetyl chloride and toluene. Schroeder and Brewster (36) recently reported, however, that HgCl_2 will catalyze the reaction between benzoyl chloride and diphenyl ether. It was our belief that diphenyl ether was sufficiently active to react with benzoyl chloride without the help of a catalyst. To test this, a run was made following exactly the work of Schroeder and Brewster in all details except that no HgCl_2 was added. The resulting product obtained was distilled under reduced pressure until about 1 ml of a neutral residue remained. This residue contained a carbonyl compound as hydrochloric acid was liberated when the residue was added to a solution of hydroxylamine hydrochloride. Further evidence of ketone formation was obtained by the formation of a solid derivative with phenylhydrazine. To say that HgCl_2 did not act as a catalyst, however, would probably be false. Although conclusive evidence was found that a ketone was formed, the yield was not nearly as large as that obtained by Schroeder and Brewster.

A continuation of this problem might well involve the use of other metallic chlorides as catalysts, principally the halides of the noble metals and the more rare elements.

Johnson (19) found the optimum ratio of moles of catalyst/moles of acetyl chloride when the reaction was carried out at elevated temperatures. It would be interesting to know if this ratio is still optimum as was assumed in the present work, except for SbCl_5 , if the reaction takes place when no heat is applied.

Constant agitation would very probably increase the yield, at least where heterogeneous reaction mixtures are involved. The exact extent of increase in yield would be desirable information.

SUMMARY

Use of the Perrier order of reagent addition in the Friedel-Crafts ketone synthesis increases the yield, and if the reaction is allowed to take place at room temperature, AlCl_3 , FeCl_3 , and TiCl_4 give yields which are larger than any previously reported for these catalysts. Those metallic chlorides which were poor or only fair catalysts, as found in previous work at Oklahoma A. and M. College, were even lower in their catalytic activity when the reaction was allowed to take place at about 25°C .

In hardly any case was the falling-off of yield observed with increasing reaction time that had been found by earlier workers.

Columbium pentachloride is reported for the first time as a catalyst for the ketone synthesis, and selenium tetrachloride as a non-catalyst.

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BIOGRAPHY

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