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KETONE SYNTHESIS

By

Peter Taketoshi Mori

Bachelor of Arts

Park College

Parkville, Missouri

1945

Submitted to the Department of Chemistry

Oklahoma Agricultural and Mechanical College

In partial fulfillment of the requirement

for the Degree of

Master of Science

1948

APPROVED BY:

_____
Chairman, Thesis Committee

_____
Member of the Thesis Committee

_____
Head of the Department

_____
Dean of the Graduate School

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ACKNOWLEDGEMENT

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INTRODUCTION

This is a continuation of the study of catalysts for the Friedel-Crafts ketone synthesis started by Wilson (38), and continued by Suguitan (34), Johnson (17), and Billmeier (4).

Many metallic chlorides have been used in this reaction, but metallic bromides, as catalysts, have been rather neglected.

It is the purpose of this work to study the effectiveness of some of the metallic bromides by following essentially the experimental procedure of Billmeier (4).

HISTORICAL

In 1877, the French chemist Friedel and his American colleague Crafts (12) discovered the famous Friedel-Crafts reaction, which now has such great industrial application (7, 13, 18, 35).

Research on this reaction has mainly employed the metallic chlorides as catalysts, and very little work has been done with the various metallic bromides, except aluminum bromide.

Thomas (35) cites some references and states, "Aluminum bromide is more active a catalyst than aluminum chloride. Aluminum bromide has been used for all the type reactions which are catalyzed by aluminum chloride; in some of the more easily effected condensations, however, aluminum chloride is preferred as a less drastic catalyst."

Zelinskii and Turova-Pollak (40) added aluminum bromide and cis-decalin to acetyl chloride. They were able to get only a very small yield of methyl naphthyl ketone because of isomerization of the decalin by the catalyst. Heldman (15) found that in the presence of aluminum bromide, methyl bromide and ethyl bromide alkylate butanes to give substantial yields of pentanes and hexanes, respectively, as well as some higher paraffins.

Menshutkin (26) observed that antimony tribromide increases the rate of benzene or its derivatives with benzoyl chloride more than does antimony trichloride catalyst.

Pajeau (31) found beryllium bromide to be inactive as a catalyst in the Friedel-Crafts ketone synthesis. However, it is active in the hydrocarbon synthesis involving the more active alkyl halides.

Holleman and his coworkers (16) found that when benzyl bromide or chloride is boiled with toluene and ferric bromide, the chief organic product is p-benzyltoluene. In similar experiments in which antimony tri-

bromide was the catalyst, no p-benzyltoluene was formed.

Suguitan (34) compared the effectiveness of aluminum bromide, titanium tetrabromide, antimony tribromide, ferric bromide, zinc bromide, tellurium tetrabromide, and stannic tetrabromide as catalysts in the Friedel-Crafts ketone synthesis. He found that the metallic bromides are poorer catalysts than the corresponding chlorides with the exception of aluminum bromide and antimony tribromide. Among the metallic bromides the order of activity was found to be: aluminum bromide > titanium tetrabromide > antimony tribromide > ferric bromide > zinc bromide > tellurium tetrabromide > stannic tetrabromide.

At an early date, Armstrong (1) suggested that the catalyzed bromination of benzene is very similar to the Friedel-Crafts reaction, for the reaction may proceed through an 1,2- or 1,4- addition to the unsaturated nucleus and an elimination of hydrogen bromide. In the absence of such catalysts as ferric bromide and other metallic halides, benzene is converted into the hexabromide by addition of bromine. The catalysts seem to promote the elimination of hydrogen bromide and a stable substitution product results.

Many researches, reviewed by Fieser (11) and Thomas (35), tend to support the conclusion that mechanisms of halogenation probably are applicable to the Friedel-Crafts reaction (12). Both reactions proceed under the catalytic effect of certain metallic halides, and hydrogen halide is a product of both substitutions.

Pajeau (30) compared the effectiveness of the bromides of beryllium, magnesium, calcium, zinc, strontium, cadmium, barium, and mercury as catalysts for the bromination of benzene. He found that beryllium was the most effective catalyst. Cadmium was observed to be less effective than berylli-

um, but more than zinc or mercury; and calcium, magnesium, barium, and strontium were found to be practically useless as catalysts.

EXPERIMENTAL

Materials Used

Catalysts

The anhydrous aluminum bromide was prepared as directed by Winter and Cramer (39) with modifications. A 500 ml. distilling flask was half filled with dry aluminum pellets, and then liquid bromine was introduced gradually near the bottom of the flask by means of a dropping funnel. The bottom of the flask was padded with glass wool to prevent the hot molten aluminum from cracking the flask. The reaction product was purified by repeated fractional distillation. The fraction coming over at 267 to 269° C. was collected. (Lit. b.p. 268° C. (19))

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

The anhydrous antimony tribromide was prepared as directed by Serullas (23) with slight modifications. Dry powdered antimony was added in small portions into a 250 ml. distilling flask containing liquid bromine, the flask being shaken after each addition. When no further reaction took place, the reaction product was purified by repeated fractional distillation. The observed boiling point was 280-1° C. (Lit. b.p. 280° C. (19))

The anhydrous ferric tribromide was prepared as directed by Kablukoff (22) and modified by Suguitan (34). Dry iron powder was heated to redness, and then dry bromine vapor was caused to pass over the red-hot metal. At first, a great deal of trouble was encountered, for the pyrex glass combustion tube melted. Later, a silica tube was used, and this enabled the reaction to take place at a much higher temperature. The ferric bromide formed was difficult to obtain free from ferrous bromide,

and may have remained contaminated with it.

Essentially the same procedure was followed in preparing molybdenum tetrabromide, tungsten pentabromide, and tellurium tetrabromide. Limitations of time did not permit analyzing catalysts for metal-bromine ratio, so that it is possible that the first two contained other polybromides than the ones named. Identification of the molybdenum tetrabromide was based on its formation in presence of excess bromine and its black color; molybdenum tribromide is greenish (24). The tungsten pentabromide formula was assigned because it is the stabler form and because the product was brown, not bluish-black like the hexabromide (25).

Cadmium bromide hydrate was merely fused in a crucible to drive off the water.

C. P. mercuric bromide from the Merck Chemical Company was used without further purification.

The anhydrous stannic tetrabromide was prepared as directed by Baumer and Krepelka (2). Liquid bromine was allowed to drip slowly into a 250 ml. distilling flask containing 40 g. of dry powdered tin. When the reaction stopped, the product was purified by repeated fractional distillations. The observed boiling point was $202\text{-}3^{\circ}$ C. (Lit. b.p. 202° C. (19))

The anhydrous titanium tetrabromide was prepared by the method of Bond and Crane (5). Gaseous hydrogen bromide was allowed to bubble through titanium tetrachloride held between 50 and 60° C. At first, the necessary hydrogen bromide was generated by allowing reagent-grade phosphoric acid to drip slowly on C. P. potassium bromide. The mixture was heated to start the reaction. The water formed was absorbed by a bubble counter containing phosphoric acid. This method was tried repeatedly, but in every trial sufficient back pressure was created to blow out the stop-

per on the generator. Perhaps enough water got through the bubble counter
to clog the gas inlet tube by hydrolyzing the titanium compounds. Finally,
the hydrogen bromide was generated by allowing liquid bromine to drip slow-
ly on naphthalene. It required considerable time--approximately forty-
eight hours--for most of the titanium tetrachloride to be converted to tita-
nium tetrabromide. The reaction mixture was purified by fractional distil-
lation. The observed boiling point was 230-1^c C. (Lit. b.p. 230° C. (19))

The anhydrous zinc bromide was prepared by heating technical-grade
zinc bromide in a inverted Y-tube with sealed legs. The bromide was dis-
tilled from one leg into the other one under reduced pressure.

The prepared catalysts were kept in glass-stoppered bottles, and the
bottles were placed in a desiccator which contained phosphoric anhydride.
This precaution was necessary, for the bromides are very hygroscopic.
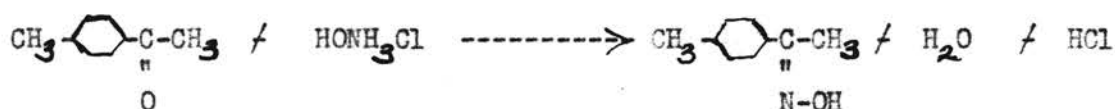
Friedel-Crafts Reagents

The acetyl bromide used was C. P. grade. It was kept in four small
bottles which were placed in a desiccator.

Merck's reagent-grade toluene was used without further purification.

Analytical Reagents

The hydroxylamine hydrochloride method modified by Johnson (17) and
used by Billmeier (4) was chosen for measuring yields of the ketone
formed. There are many other quantitative determinations of ketones in the
literature, but they are, in general, much less suitable for this work.

The hydroxylamine hydrochloride method (3) consists in titrating the
hydrochloric acid liberated in the following reaction:

$$CH_3 \bigcirc \underset{O}{\overset{\text{"}}{C}}-CH_3 \ + \ HONH_3Cl \ ----------> \ CH_3 \bigcirc \underset{N-OH}{\overset{\text{"}}{C}}-CH_3 \ + \ H_2O \ + \ HCl$$

The approximately 0.5 N solution of hydroxylamine hydrochloride was prepared by dissolving 75 g. of C. P. hydroxylamine hydrochloride in a small amount of absolute methanol and then diluting to 2000 ml. with the same solvent.

The indicator used was butter yellow, prepared by dissolving p-dimethylaminoazobenzene in C. P. methanol.

The sodium methoxide solution was prepared by dissolving approximately 10 g. of dry clean sodium in four liters of C. P. methanol. This solution was standardized against a known weight of potassium acid phthalate and found to be 0.1072 N. Later, two liters of this solution were made more concentrated by adding more sodium, and this more concentrated solution was determined to be 0.5384 N. The stronger solution of sodium methoxide was desirable, for some of the catalysts gave high yields of ketone, and in order to use a smaller volume of the sodium methoxide solution, a more concentrated solution was required.

PROCEDURE

As in previous theses, toluene was the aromatic compound used, for it is cheap and easy to obtain and keep in pure form. It also gives good yields of ketone. Toluene does not give as high yields of ketone as anisole, but it has the advantage of not reacting at all in the absence of catalysts.

Before the bromide catalysts were tested, trial runs were made with aluminum chloride and acetyl chloride to find out whether the conditions chosen for the comparison would give as good yields as obtained with the chlorides by Billmeier (4).

Since the results were satisfactory, the procedure as described by Billmeier (4) was followed with slight modifications. Suguitan (34) used acetyl chloride in his investigation, but in this work acetyl bromide was used. Instead of the 250 ml. long-neck flask employed by Billmeier, a round-bottomed 50 ml. flask with a 19/38 ground-glass joint was used as the reaction vessel. Into the flask, previously dried for several hours in an oven at 110° C., was placed 1 ml. of acetyl bromide previously cooled to $10\text{-}15^{\circ}$ C. and pipetted at that temperature. It was established by separate calibration that the pipette delivered 1.62 ± 0.01 g. under these conditions, and that the error due to temperature variation was less than the experimental error of the rest of the procedure. The catalyst was then added to the flask. Several molar ratios of catalyst to acetyl bromide were used (1:1, 1.5:1, 2:1, 3:1, and 4:1). It was necessary to reduce the amounts of certain catalysts used, for they formed large volumes of very insoluble hydroxides which made steam distillation of the ketone difficult. Liquid catalysts were added by employing a graduated pipette, while solids were weighed out quickly to the nearest centigram on glazed paper and transferred immediately to the reaction flask.

Excess of chilled toluene, approximately 10 ml., was added to the reaction flask. The reaction flask was kept in an ice bath until all the reactants had been added, for the addition of active metallic bromides to acetyl bromide usually results in the exothermic formation of a molecular complex. The heat, if not removed, may volatilize some of the acetyl bromide, and this would give inaccurate yields of ketone.

After all the reactants had been added to the flask, it was stoppered, placed in a mechanical shaker, and shaken for the desired length of time at room temperature (25-35° C.). Usually four such flasks were shaken at the same time. When the molar ratios of 1:1, 1.5:1, and 2:1 were used, the reaction time was two hours. This time was chosen as a convenient standard, since we were not primarily interested in studying the effect of varying the reaction time in this work. Another reason for the choice came from Billmeier's data. His graph shows that good catalysts will usually give a maximum yield of ketone in two or three hours. The reaction time of four hours was used along with molar ratios of 3:1 and 4:1. This was done to see how exhaustive treatment, with both more catalyst and longer reaction time, would affect the yield of ketone.

At the end of the reaction time, water was added to the reaction flask to hydrolyze the catalyst and unreacted acetyl bromide and thereby stop the reaction.

C. P. grade potassium hydroxide pellets were added to the hydrolyzed mixture until the base was in excess as indicated by phenolphthalein.

The excess toluene and the p-methylacetophenone were distilled with steam. The steam was passed directly into the reaction mixture through a glass tube which ran from the steam generator through the connecting joint by way of a ring seal down into the liquid.

Approximately 75 ml. of distillate was collected in a separatory fun-
nel. Just prior to the end of the distillation, water was allowed to drain
from the condenser. This allowed the steam to sweep out any ketone which
might be adhering to the walls of the condenser. A pellet of potassium
hydroxide was added to the distillate to be sure that no acid was present
in the distillate. To the distillate approximately 15 g. of C. P. sodium
nitrate was added to salt out the product. It was found that technical-
grade sodium nitrate contained some impurity which interfered with the
salting-out process. The toluene-ketone layer was carefully separated from
the water solution, and two more extractions were made using approximately
5 ml. portions of benzene. The extracts were placed in a glas-stoppered
bottle, to which 20 ml. of the approximately 0.5 N solution, neutral to
butter yellow indicator, of hydroxylamine hydrochloride in absolute methyl
alcohol were added.

The solution being analyzed was allowed to stand for about twenty-
four hours before the first titration was made, for the reaction between
p-methylacetophenone and hydroxylamine hydrochloride is slow and does not
go to completion readily. The hydrochloric acid liberated in the reaction
was titrated with the standard sodium methoxide solution. The first end
point reached was not always permanent, so the titration was repeated at
intervals of twenty-four hours until the permanent end point was reached.

TABLE OF RESULTS

Variation of Yield with Kind and Amount of Catalyst

Catalyst	Moles catalyst/mole acetyl bromide	Time (hours)	Yield of ketone (%)
Aluminum chloride	1.6[1]	1/4	77.3, 77.3
		2	75.9, 77.7
		3	77.3, 76.5
Aluminum bromide	1	2	82.4
	1.5	2	83.9
	2	2	81.6
	3	4	79.3
Ferric bromide	1	2	37.3
	1.5	2	41.2
	2	2	47.5, 48.5
	3	4	59.0, 63.2
Antimony tribromide	1	2	0.6
	1.5	2	2.8
	2	2	9.2, 9.8
	3	4	28.8, 25.5, 27.0
	4	4	1.5, 2.1, 1.9

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[1] Acetyl chloride was used instead of acetyl bromide for the run with aluminum chloride catalyst.

TABLE OF RESULTS

(continued)

Catalyst	Moles catalyst/mole acetyl bromide	Time (hours)	Yield of ketone ($\%$)
Zinc bromide	1	2	2.6
	1.5	2	3.9
	2	2	4.1, 7.1, 7.0
	3	4	15.2, 17.6, 17.7
	4	4	14.2, 17.8, 17.5
Titanium tetrabromide	1	2	3.6, 3.3
	1.5	2	4.6, 4.8
	2	2	11.8, 12.1
	3	4	7.3, 7.7, 8.1
Tellurium tetrabromide	1	2	1.5, 1.0
	1.5	2	1.1, 0.8
	2	2	0.9, 1.0
	3	4	2.6
	4	4	3.8
Molybdenum tetrabromide	1	2	1.8
	1.5	2	3.4
	2	2	2.8
	3	4	0.0, 0.0

TABLE OF RESULTS

(continued)

Catalyst	Moles catalyst/mole acetyl bromide	Time (hours)	Yield of ketone (%)
Tungsten pentabromide	1	2	0.8
	1.5	2	0.8
	2	2	1.5
	3	4	0.8
Cadmium bromide	1	2	0.9
	1.5	2	1.0
	2	2	0.8
	3	4	0.6
	4	4	0.7
Mercuric bromide	1	2	0.4
	1.5	2	0.3
	2	2	0.2, 0.15
	3	4	0.7, 0.8
	4	4	0.3, 0.3
Stannic tetrabromide	1	2	0.4, 0.4
	1.5	2	0.3, 0.5
	2	2	0.3, 0.15
	3	4	0.3, 0.2

Figure 1

The reaction time was 4 hours, when 3 to 4 moles of catalyst used, and it was 2 hours for the others.
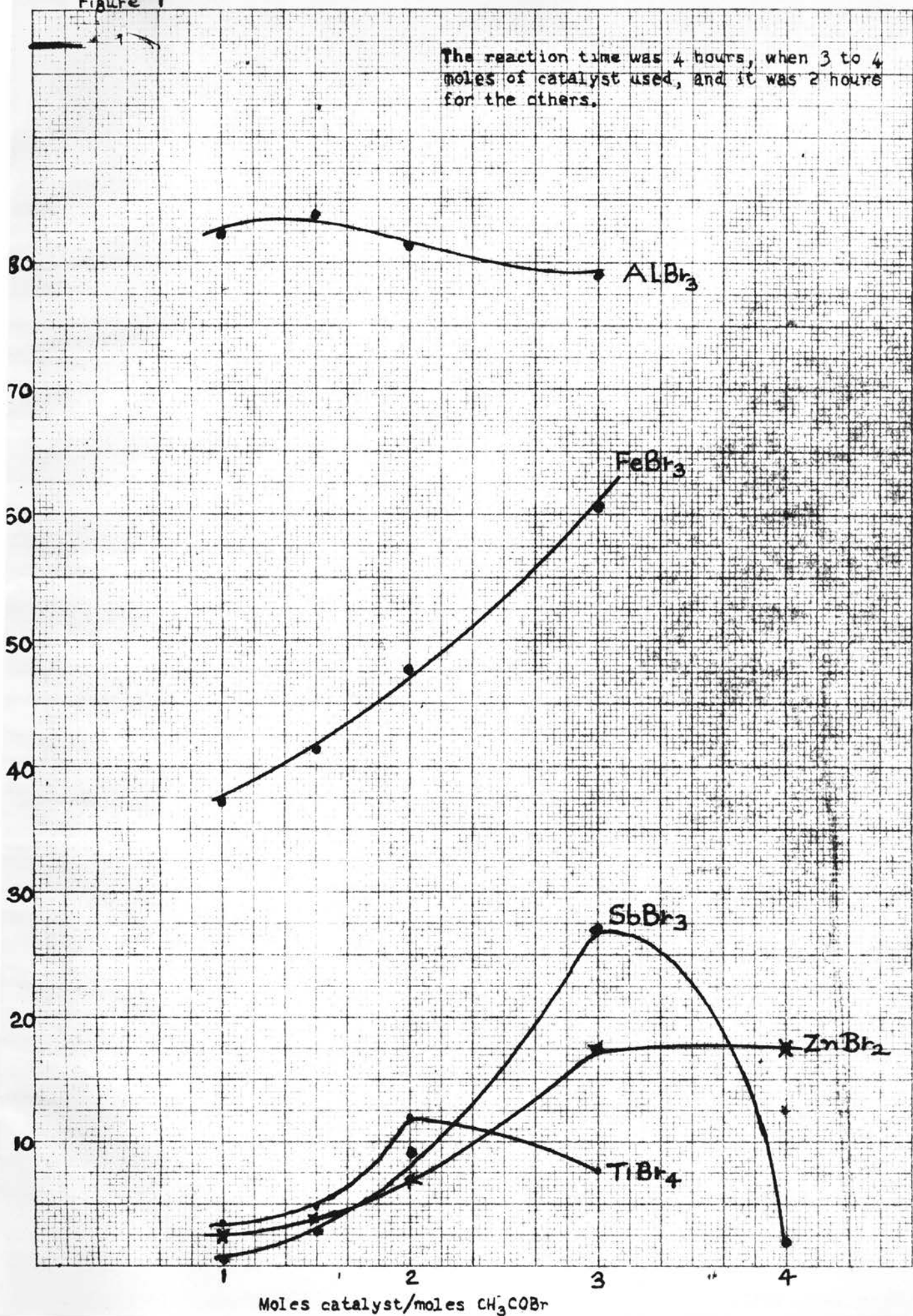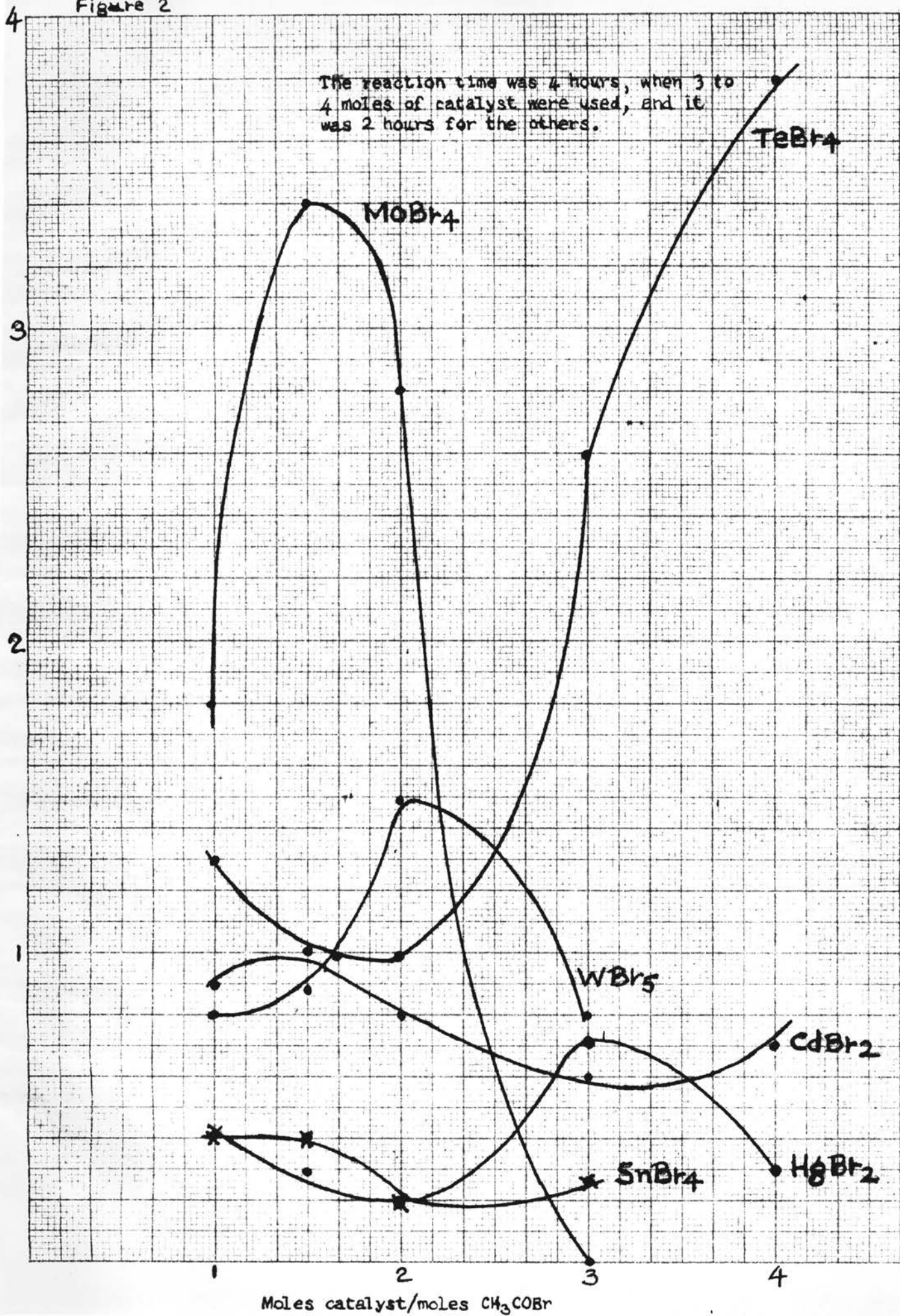

Moles catalyst/moles CH_3COBr

Figure 2

The reaction time was 4 hours, when 3 to 4 moles of catalyst were used, and it was 2 hours for the others.

TeBr₄

MoBr₄

WBr₅

CdBr₂

SnBr₄

HgBr₂

Moles catalyst/moles CH₃COBr

DISCUSSION OF RESULTS

It is first of interest to compare results with those in the litera-
ture, insofar as that is possible. The 77-83% yields of p-methylacetophe-
none here obtained with aluminum chloride and aluminum bromide are as good
as reported anywhere for this particular synthesis. Laboratory manuals (9)
claim 50-60% yields of acetophenone by classical methods, but Norris and
Wood (28) obtained 72% from benzene $\neq$ acetyl bromide $\neq$ aluminum chloride
and 76% from benzene $\neq$ acetyl chloride $\neq$ aluminum bromide. Sorge (33) re-
ported 70% yields of p-methylacetophenone via the Perrier procedure using
aluminum chloride, and Verley (36) 80% by operating at 0° C. and removing
the evolved hydrogen chloride under reduced pressure. In previous theses
of this series, Johnson (17) obtained a maximum of 70-71% for aluminum
chloride, used in boiling toluene, and Billmeier (4) 73-74% via the Perrier
procedure and room-temperature reaction. In contrast to these yields, 96-
98% of the theoretical amount of benzophenone can be made by the Friedel-
Crafts reaction. We must conclude that the alkyl aryl ketones, being more
susceptible to aldol-type condensations induced by hydrogen chloride, can-
not be expected in such semiquantitative yields.

A defense of the technique, used in this work, of performing the Frie-
del-Crafts reaction in sealed containers is desirable, since Verley (36),
Groggins (13), and doubtless others have thought the removal of hydrogen
halide desirable or even essential to maximum yield. Groggins has in fact
supplied experimental data to show a 3-4% improvement in yield of 4'-chloro-
2-benzoylbenzoic acid when hydrogen chloride was swept out as produced.
This procedure is based on conceiving the Friedel-Crafts reaction as rever-
sible, so that removal of hydrogen chloride would "shift the equilibrium"
in favor of ketone. Removal of the acid would also reduce its aldol-con-

densation effect on the ketone, but since the metallic halides are also condensing agents, this factor is probably unimportant.

Against removal of hydrogen chloride three arguments may be advanced. First, it complicates the experimental procedure, especially when a volatile acid chloride is being used. Second, benzophenone is not cleaved by hydrogen chloride in presence of aluminum chloride to yield benzoyl chloride and benzene (29). In other words, this Friedel-Crafts reaction is not reversible. Reversibility is well known for the hydrocarbon synthesis, including the addition of aromatic nuclei to certain olefins (35), but probably is not appreciable in the ordinary ketone synthesis. Third, hydrogen chloride is known to activate aluminum chloride acting as a catalyst and thus to favor the reaction; indeed, Thomas (35) suggests that the real catalyst is not aluminum chloride, but hydrogen tetrachloroaluminate.

The Table of Results presents experimental data on the comparative efficiencies of various catalysts.

Except for stannic tetrabromide, Suguitan's results (34) show lower yields as compared to those obtained in this work. The inferiority of the yields he obtained may be due to several reasons. First of all, he did not use the Perrier method of reagent addition. Billmeier (4) discusses the advantages of the Perrier method in his research work. In the Perrier method all of the acid halide is combined in a non-volatile addition compound, and therefore the danger of losing some acid halide is greatly lessened.

Carrying out the reaction at the boiling point of water may have also produced smaller yields. Billmeier (4) found that certain catalysts gave poorer yields at higher temperatures. It is very probable that at higher temperatures some catalysts will cause self-condensation of the ketone (8),

thereby decreasing the yield.

Another reason for Suguitan's lower yields (34) may be that he used
only 1.1 moles of catalyst for 1 mole of acetyl chloride. In this work,
as stated earlier, 1.0, 1.5, 2.0, 3.0, and 4.0 moles were used. It is diffi-
cult to say that 1.1 moles was not the optimum amount at the temperature used
by Suguitan in his research, but it is unlikely that all catalysts would have
the same optimum ratio.

Shaking the flask may have some bearing on the yield, but since Suguitan
did reflux his reactants, the results here probably are not greatly affected
by it. However, mechanical shaking probably does help in increasing the
yield produced by the less soluble catalysts.

Suguitan (34) also used acetyl chloride as one of the Friedel-Crafts
reagent. Although aluminum chloride has frequently been used in preparative
work along with alkyl or acyl bromides, there is no way of determining the
true effectiveness of catalysts if the catalyst and the organic halide con-
tain different halogens. Using acetyl chloride with metallic bromide cata-
lysts probably has the same effect as employing mixed chloride-bromide cata-
lysts; see Norris and Wood (28) on this exchange.

Suguitan (34) found the order of activity of the bromides to be: alu-
minum bromide > titanium tetrabromide > antimony tribromide > ferric bro-
mide > zinc bromide > tellurium tetrabromide > stannic tetrabromide. In
this work, the order of activity was as follows: aluminum bromide > ferric
bromide > antimony tribromide > zinc bromide > titanium tetrabromide > te-
llurium tetrabromide > molybdenum tetrabromide > tungsten pentabromide >
cadmium bromide > mercuric bromide > stannic tetrabromide.

Anhydrous aluminum bromide was the best catalyst tested; the 80-84%
yield obtained with aluminum bromide is about twice as good as the 37-63%

yield with ferric bromide. The antimony tribromide catalyst showed 26-29%
yield when three moles of catalyst were used, but 1.5-2.1%—a very conspicu-
ous loss in yield—when four moles were used. This behavior of antimony tri-
bromide agrees with the observations of Menshutkin (26), who found that with
increasing amounts of antimony tribromide resinification and decomposition
became very apparent. Similar but smaller decreases were shown by titanium
tetrabromide and molybdenum tetrabromide. However, zinc bromide and ferric
bromide do not show this abrupt drop in yield. In fact, the results with
ferric bromide show that a maximum was never reached. This is attributed to
its impure state; the difficulty of purification has already been mentioned.
If the impurity, ferrous bromide, is inert, as seems likely, the apparent
effectiveness of the ferric bromide would be decreased. The yields obtained
with aluminum bromide, ferric bromide, antimony tribromide, zinc bromide,
and titanium tetrabromide are much better than those from most of the bro-
mide catalysts tested. All the rest were poor, especially stannic tetrabro-
mide.

Pajeau (30) found cadmium bromide to be better than zinc bromide in the
bromination of benzene. In this work, the zinc bromide was found to be the
better catalyst. However, the poor yield of ketone obtained in this work by
using the cadmium catalyst may be due to the lack of purity of the catalyst
itself. Nevertheless, mercuric bromide was also found to be a very poor
catalyst in this work. Pajeau found zinc bromide to have about the same ac-
tivity as mercuric bromide.

The effectiveness of the catalysts cannot be correlated with the solu-
bility of these metallic bromides in the organic mixture, for the results
show no apparent relationships between these factors. Wertyporoch and Fir-
la (37) found aluminum chloride to be a better catalyst than aluminum bro-

mide, when excesses of ethyl chloride and ethyl bromide were used to poly-
alkylate benzene with these two catalysts, respectively. They suggest that
the lower yields were obtained with the aluminum bromide combination probably
because aluminum bromide is more soluble in the ethyl bromide-hydrocarbon
mixture and therefore may bring about the dealkylation of some of the hexa-
ethylbenzene formed.

In the ketone synthesis, on the other hand, Olivier (29) found that
aluminum bromide was a better catalyst than aluminum chloride for the action
of benzoyl halides on benzene. He also observed that the velocity of the
reaction with benzoyl bromide is considerably greater than with benzoyl
chloride. Norris and Wood (28) observed aluminum bromide to have slightly
more catalytic activity than aluminum chloride in the ketone synthesis. We
have also found aluminum bromide to give higher yields of ketone.

Billmeier (4) observed the metallic chlorides to have the following
order of activity: aluminum chloride > ferric chloride > columbium penta-
chloride > antimony pentachloride > titanium tetrachloride > molybdenum
pentachloride > stannic tetrachloride > tellurium tetrachloride >> beryllium
chloride > zinc chloride > bismuth trichloride. To repeat, the order now
found for the bromides is: aluminum bromide > ferric bromide > antimony tri-
bromide > zinc bromide > titanium tetrabromide > tellurium tetrabromide >
molybdenum tetrabromide > tungsten pentabromide > cadmium bromide > mercuric
bromide > stannic tetrabromide. It is obvious that the positions of the ha-
lides of zinc, molybdenum, and tin are different in the two series. The
only metallic bromides which gave better yields of ketone than the corres-
ponding chlorides are aluminum bromide, zinc bromide, and antimony tribromide.[2]

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[2] Antimony trichloride has been reported (10) to be a non-catalyst. How-
ever, it was tested in refluxing toluene, in which it is probably more soluble

In general, the metallic chloride catalysts gave much higher yields of ketone in this particular Friedel-Crafts synthesis. Billmeier did not test the chlorides of tungsten, cadmium, or mercury, so again no certain comparison can be made, although cadmium chloride and mercuric chloride have been reported (10) non-catalysts.

This is the first time that molybdenum tetrabromide, tungsten pentabromide, cadmium bromide, and mercuric bromide have been reported as catalysts for the Friedel-Crafts ketone synthesis.

Numerous suggestions can be made for future work in the study of catalysts for the Friedel-Crafts reaction. First, more bromides can be tested. Columbium pentabromide probably would be the first one to test, for its corresponding chloride gave good results. Uranium tetrabromide, zirconium tetrabromide, and gallium tribromide are also possibilities. It would also be interesting to test all those bromides which are supposedly non-reactive, for there is no proof that metals whose chlorides are inactive also have inactive bromides.

The earlier chloride-catalyst research could advantageously be repeated in the presence of added hydrogen chloride, and the bromides could be run with added hydrogen bromide.

The oxyhalides, both oxychlorides and oxybromides, need to be studied.

The use of mixed catalysts in the Friedel-Crafts ketone synthesis is worth consideration. It should be mentioned that there are two types of mixed catalysts: mixed halides of the same metal and mixed halides with

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than antimony tribromide. Quite possibly a small yield was formed and then destroyed again, to judge by our experience; it must be tried at room temperature before valid comparison can be made.

different metals but the same halogen. It has been mentioned earlier that studies on mixed halides of the same metal would have very little value, so the work with mixed catalysts should go in the direction of the mixed-metal halides. Boswell and McLaughlin (6) found that the maximum amount of hydrogen chloride was evolved in the reaction of benzene with chloroform when an equimolecular mixture of aluminum chloride and ferric chloride was used. Miller (27) observed that a mixed catalyst consisting of aluminum chloride contaminated with a little ferric chloride had less catalytic activity than pure aluminum chloride in the preparation of ω-chloroacetophenone. Groggins, Stirton, and Newton (14) found such aluminum chloride as good as a colorless, purer grade for the preparation of 4'-bromo-2-benzoylbenzoic acid. However, in the preparation of alkyl aryl ketones the use of a purer aluminum chloride not only gave better yields but also afforded a quicker and cleaner separation of the oily ketonic layer from the hydrolyzed reaction mass. Riddell and Noller (32) reported that in the preparation of alkyl phenyl ketones from acid chlorides and benzene, the yields diminished as aluminum chloride was replaced by ferric chloride. On the contrary, Martin, Pizzolato, and McWaters (21) observed that in the preparation of p-methylbenzophenone the yields increased with increasing percentage of ferric chloride. They also investigated the reaction of benzyl chloride with toluene and found that the velocity increased greatly in the presence of very small percentages of ferric chloride along with the aluminum chloride, but decreased again when substantial amounts of ferric chloride are present.

It would also be interesting to study Lewis acids in general for the ketone synthesis and find how far acidity correlates positively with Friedel-Crafts catalytic power. Luder and Zuffanti (20) suggest this, but consecutive reactions might make it difficult to settle the question.

SUMMARY

In comparing metallic bromides as Friedel-Crafts catalysts, the Perrier method of combining reagents was employed, and the use of mechanically shaken stoppered reaction flasks were introduced.

The yields of p-methylacetophenone were much higher in this study than in the work of Suguitan (34). Stannic tetrabromide was the only catalyst that gave lower yields in the Friedel-Crafts ketone synthesis.

Among the bromides the order of activity was observed to be: aluminum bromide > ferric bromide > antimony tribromide > zinc bromide > titanium tetrabromide > tellurium tetrabromide > molybdenum tetrabromide > tungsten pentabromide > cadmium bromide > mercuric bromide > stannic tetrabromide. The bromides of aluminum, antimony, and zinc were found to have better catalytic activity than the corresponding chlorides. This is the first time that molybdenum tetrabromide, tungsten pentabromide, cadmium bromide, and mercuric bromide have been reported as catalysts for the Friedel-Crafts ketone synthesis.

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BIOGRAPHY

Peter Taketoshi Mori was born at Montebello, California, February 16, 1925. He received his grade school training in the same city. In June 1942 he was graduated from Montebello High School, and in September of the same year he entered Park College, Parkville, Missouri and received the degree of Bachelor of Arts in June 1945.

He entered the graduate school of Oklahoma A. and M. College in September 1945 where he has been employed as a research assistant in the Department of Chemistry until the present time.

Typed by:

Peter Taketoshi Mori

Stillwater, Oklahoma