

Chem. Thesis case



The Application of Friedel and Craft Condensation
to Non-Benzenoid Hydrocarbons.

by

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I wish to express my sincere thanks and gratitude to Professor J. F. Norris under whose supervision this investigation was carried out, for his constant advice and kind cooperation throughout the work. I am glad to gratefully acknowledge the financial aid awarded to me by the Institute in the shape of a Graduate Scholarship during the years 1920-1922.

Respectfully submitted

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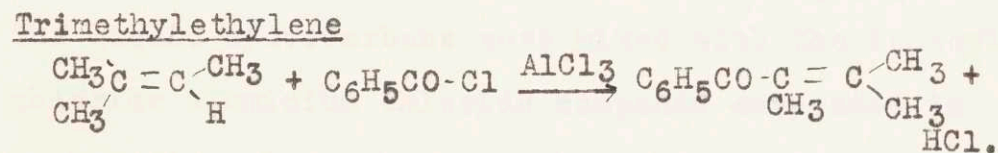
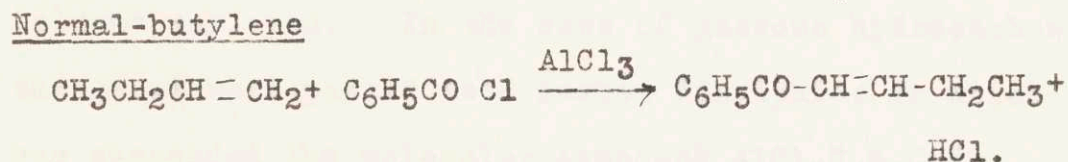
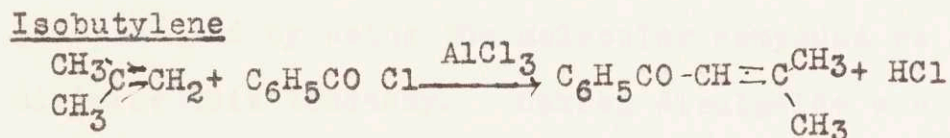
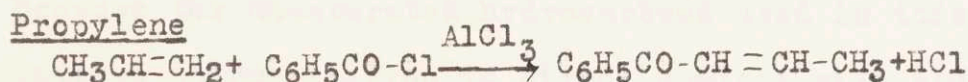
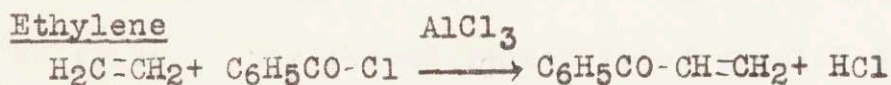
The object of this research was to study the action of benzoyl chloride upon non-benzenoid hydrocarbons in the presence of anhydrous aluminium chloride. Such a study will help us to understand the influence of unsaturation or alkyl radicals upon the activity of hydrogen atoms in organic compounds. A better knowledge of the character of unsaturated hydrocarbons is of great importance, because of their similarity to benzene and of the fact that some of the industrial processes, such as cracking of oils, yield the higher olefines as by-products. The theoretical possibilities of the Friedel and Crafts condensation when applied to such hydrocarbons with suitable alkyl or acyl chlorides are very stimulating to further research.

The plan of work and results obtained.

The methods of procedure adopted in this piece of work are based upon the results obtained by Professor J. F. Norris¹ and his students in a previous investigation where they have definitely shown that ethylene does react

¹J.F.Norris and H.B.Couch. J.A.C.S. Vol.XLII.No.11.(1920)

with benzoyl chloride, in the presence of anhydrous aluminium chloride, yielding phenyl-vinyl ketone. In our experiments we have made a further study of ethylene and the higher hydrocarbons propylene, isobutylene n-butylene, & trimethyl ethylene, and obtained the corresponding unsaturated ketones. We can represent them by the following chemical equations.



Attempts were also made to carry on a similar condensation with styrol, diisopropyl and ethyl malonate. No definite results were obtained. Styrol polymerized into a hard mass on coming into contact with aluminium

chloride and benzoyl chloride compound. Diisopropyl gave a product which does not, however, have the properties of the corresponding ketone expected. Ethyl malonate also did not give the ketone that we expected.

Benzoyl chloride was chosen for two reasons. The first is its great reactivity and the second is the fact that it forms a molecular compound¹ with aluminium chloride. The second reason is of special importance because the unsaturated hydrocarbons used in this work undergo polymerization in direct contact with aluminium chloride and by using the molecular compound we could minimize this tendency. Carbon disulphide was the solvent employed. In the case of gaseous hydrocarbons the gases were passed into carbon disulphide in which was suspended the molecular compound $\text{AlCl}_3\text{C}_6\text{H}_5\text{COCl}$. The liquid hydrocarbons were mixed with the benzoyl chloride aluminium chloride compound suspended in carbon disulphide which was kept in a flask fitted with a reflux condenser. The products of the reaction were treated in the usual way and the ketones were obtained in as pure a state as possible. The ketones which have been described in the literature were identified by their boiling points and the properties of the

1. G. Perrier. *Compte Rendu*. 116 1298-1300. (1893)

were phenyl hydrazones/prepared from them. The more important results are summarised below.

Ethylene: The reaction product was a yellow oil having a piercing odor. It showed the presence of halogen by copper wire test. Therefore it was treated with alcoholic potash and the oil free from halogen was obtained. It boils at 115° under diminished pressure (ao mm). With phenyl hydrazine it forms a compound which crystallizes in yellow needles which melt at 151° . This proves it to be a ketone. The bromine reaction proves its unsaturation. Dry hydrogen chloride reacts with it forming a solid which melts at 51° . These facts show that the oil is phenyl vinyl ketone which has been prepared by Professor E. P. Kohler¹ in a different way and whose properties agree with those described above. In addition to the oil a solid by-product is formed which melts at 105° .

Propylene: The reaction product was a colorless oil and showed presence of chlorine. It was treated with alcoholic potash. The resulting oil boils at 135° under 20 mm pressure. The compound which it forms with phenyl hydrazine melts at 108° and forms a fluorescent solution in alcohol. It decolorizes bromine forming

1. E.P.Kohler Am.Chem.Jour.42 375. (1909).

a solid dibrom compound. These properties correspond with those of the propenyl phenyl ketone ($\text{CH}_3\text{CH}=\text{CHCO}-\text{C}_6\text{H}_5$) which was prepared by Kohler¹ by another method. By the action of hydrogen chloride this ketone forms a red oil which is unstable.

Isobutylene: The major part of the condensation product boiled at 139° - 142° at 18 mm. and formed a phenyl hydrazone which melts at 86° - 87° . Professor Kohler¹ prepared by another method the Ketone of the structure $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} > \text{C} = \text{CHCO}-\text{C}_6\text{H}_5$. He found it to boil at 148° at 22 mm. and to give a phenyl hydrazone which melted at 88° .

Normal butylene: The reaction product is a yellow oil with a pleasant odor. It has traces of chlorine. By treatment with alcoholic potash it was freed from chlorine and the purified product yielded two fractions which boil within 15° of each other. The first fraction boils at 99 - 102 at 5 mm and the second boils at 115 - 122 at 5 mm. The phenyl hydrazone of the first fraction was prepared and it melts at 130° - 131° .

Trimethyl ethylene: The condensation product contained chlorine and therefore was treated with alcoholic potash. The purified product was a colorless oil of pleasant odor and boils in two fractions. The first

¹E.P.Kohler.Amer.Chem.J.42. 375 (1909).

fraction boils at 120°-132° at 11 mm and the second boils at 135°-132° at 11 mm. The phenyl hydrazones of the two fractions were prepared, each of which melted at 127° and the mixture of the two also melted at 127°.

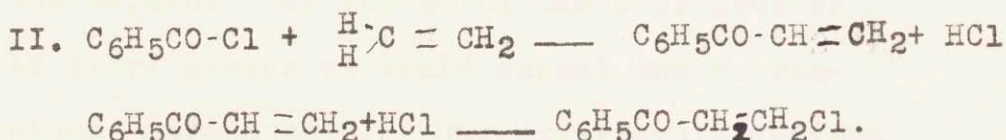
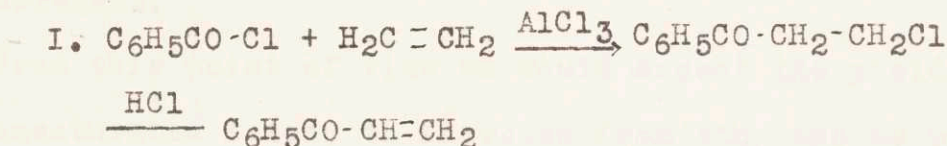
Note:

Diisopropyl was selected for a condensation to test if the tertiary carbon had any activating influence upon the hydrogen. The fact that we obtained a condensation product which on analysis showed the presence of oxygen indicates that some reaction must have taken place.

Ethyl malonate was chosen to test if the two adjoining carbonyl groups would activate the hydrogen linked to the intermediate carbon. The fact that malonic ester could be nitrated led Professor Norris to suggest this condensation to me. Although we have not identified the reaction product its large yield and high boiling point show that there is material enough for further research.

Discussion.

The fact that the unsaturated hydrocarbons yield the condensation products that are expected, is in accordance with the notions of the activating influence of the double bonds in organic compounds. There is uncertainty however about the mechanism of the condensation because of the presence of a compound containing chlorine in each of the reaction products. The reaction may take place in either of two ways which are illustrated by the following formulae.



Attempts were made to find out if the β chlorpropio-phenone ($\text{Cl}\cdot\text{CH}_2\text{CH}_2\text{CO}\cdot\text{C}_6\text{H}_5$) could be isolated from the crude reaction product of ethylene condensation. But they were not successful. This may be due to the solubility of the β chlor propiophenone in the phenyl vinyl ketone. The experiments of H.E. Wieland¹ on the action of nitric acid

upon ethylene and substituted ethylenes have shown that nitric acid is first added to the unsaturation and then by the loss of water the nitro compound is formed. Therefore, it is not improbable that the reaction represented by formula I may be the correct one.

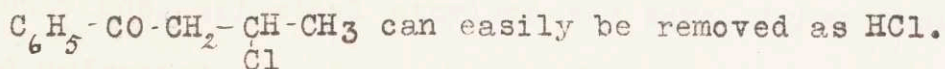
The choice of the hydrocarbons was based upon two important considerations.

- (1) Influence of positive or negative groups, and unsaturation, upon the activity of hydrogen in organic compounds.
- (2) Stability of the compounds as its molecular weight increases or as the number of positive groups increases.

From this point of view we would expect the yield of the unsaturated ketone to increase from ethylene as we go up in the series. By replacing the hydrogens of ethylene by alkyl groups we would expect the corresponding ketones more stable. Our experiments confirm both these expectations. The ketone obtained from trimethyl ethylene has one more alkyl group than that obtained from isobutylene. Again the ketone obtained from isobutylene has one more alkyl group than that obtained from propylene. This latter has in turn one more alkyl group than that from ethylene. The stability of the ketones and the yields are in the descending order from trimethyl ethylene
down

to ethylene. The properties of the ketone from propylene correspond to those of the compound $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$; which shows that it is the end hydrogen that is reactive.

The addition of hydrogen chloride to the unsaturated ketones shows very interesting results. Phenyl vinyl ketone on being treated with dry hydrogen chloride forms the β chlor propiophenone $\text{Cl}\cdot\text{CH}_2\text{CH}_2\text{CO}\cdot\text{C}_6\text{H}_5$. This chlor compound is a very stable solid, that is not affected by alkali, and that is easily volatile with steam. But propenyl phenyl ketone and the other ketones only give a deep red solution, when dry hydrogen chloride is passed through them. In the case of the red liquid obtained with propenyl phenyl ketone, we can recover the unsaturated ketone by merely treating it with water. This may be due to the fact that chlorine attached to a secondary carbon as in the compound β chlor butyrophenone



If according to the theory of Kekule¹ we regard benzene as having double bonds, its similarity to unsaturated hydrocarbons may lead us to interpret certain reactions in aromatic compounds according to the known facts in the field of olefine hydrocarbons. In this particular investigation a clear understanding of the mechanism of the reactions involved will be of great use in explaining the Friedel and Craft condensation.

Historical resumé of the work relating to the present investigation.

The peculiarities of some of the reactions in organic chemistry have led modern investigators to inquire into their mechanism. The stereo chemistry of carbon compounds and the theory of positive and negative character of certain groups have been of great use in such a study. The greater activity of the aromatic compounds as compared with that of the saturated aliphatics has been explained in various ways. One of them is that this reactivity of benzene is due to its supposed unsaturation.

S. Krapivin² effected the condensation of acyl halides with unsaturated hydrocarbons in the presence of aluminium halides. He worked with ethylene propylene, isobutylene, trimethyl ethylene and some higher unsaturated hydrocarbons. In each case he obtained the corresponding unsaturated ketone. The best conditions were to carry out the reaction in presence of a solvent, usually carbon disulphide, and at a low temperature. The boiling points and yields of the ketones were as follows:

². Chem. Zent. (1910) I. 1335.

Ketone	B.P.	Yield
$\text{H}_2\text{C}=\text{CH}-\text{CO}-\text{CH}_3$	$78^\circ - 80^\circ$	not shown
$\text{CH}_3-\text{CH}=\text{CH}-\text{CO}-\text{CH}_3$	$122^\circ - 123^\circ$	"
$(\text{CH}_3)_2\text{C}=\text{CH}-\text{CO}-\text{CH}_3$	$129^\circ - 130^\circ$	30 %
$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)-\text{CO}-\text{CH}_3$	$144^\circ - 145^\circ$	20 %

Krapavin isolated as products of subsidiary reactions, halogen substituted saturated hydrocarbons of the series $\text{C}_n\text{H}_{2n}\text{X}$ where X is the halogen and proved the existence of halogen substituted ketones of the formula $\text{C}_n\text{H}_{2n}\text{XCOCH}_3$

A number of other investigators have worked on the action of ethylene on benzene in presence of aluminium chloride¹ and also on the tendency of the unsaturated hydrocarbons to polymerize in presence of aluminium halides².

None of these investigators have attempted to put forth any theory to explain the experimental results. These facts, however, seem to lend strong evidence in favor of the theory of the activating influence of the double bond.

Such considerations as the equality in the order of magnitude of the ionization constants of benzoic acid and

1. Bull Soc. Chim. (2) 31 (529-542)

2. J.A.C.S. 38, 1384 (1917)
 ibid 39, 1420 (1917)
 Gustavson J.Pr.(27,34) 161.

acrylic acid, the equal stability of phenyl bromide and vinyl bromide and the similarity in the reaction of hydrogen chloride with benzyl alcohol and allyl alcohol led Professor J. F. Norris¹ and his students to apply Friedel and Craft condensation to ethylene. The fact that they succeeded in effecting the condensation and obtained vinyl phenyl ketone showed the similarity in the reactivity of hydrogen in benzene and ethylene.

Professor H. E. Wieland² and his students have studied the similarity between benzene and the aliphatic unsaturated hydrocarbons from another point of view. Nitration being a typical reaction in aromatic series they made experiments on the action of nitric acid upon ethylene and substituted ethylenes. They found the interesting fact that the nitric acid added itself to the ethylene double bond and formed the nitro alcohol which split off water and gave the so-called nitro-compound. This tendency to split off water depended upon the nature of the groups in the substituted ethylenes. In the case of ethylene he found the nitro-alcohol was very unstable and only the nitroethylene could be isolated.

Trimethyl ethylene also behaves in the same way. But with diphenyl ethylene he found that the

1. J. A. C. S.

2. B. 53. 201-210 (1920)

B. 54 1770 (1921).

nitro alcohol was so stable that it was difficult to prepare the corresponding nitro ethylene.

The identification of the ketones prepared in the present work has been greatly facilitated by the fact that some of them have been made by a different method¹ and their structure and properties well established.

Prof. E. P. Kohler prepared vinyl phenyl ketone, propenyl phenyl ketone and isobutenyl phenyl ketone by the following methods.

Vinyl phenyl ketone: Allyl alcohol was treated with bromine and the resulting dibrom alcohol was oxidised by nitric acid to dibrom propionic acid. The acyl chloride of this acid was prepared by the action of phosphorus trichloride. By the Friedel and Craft condensation of this acid chloride with benzene he obtained dibrom propiophenone and by treating the latter with potassium iodide and alcohol he prepared vinyl phenyl ketone.

He describes this as a highly unsaturated yellow oil, with a piercing odor and great tendency to polymerize. Its boiling point was 115° at 20 mm. By treating the ketone with phenyl hydrazine he prepared a compound which crystallized in yellow needles and melted at 158°. By saturating the vinyl phenyl ketone with hydrochloric acid he also obtained chlorpropiophenone which crystallized

1. E.P.Kohler. Amer.Ch.Jour. 42 375-401 (1909)

in plates and melted at 57°.

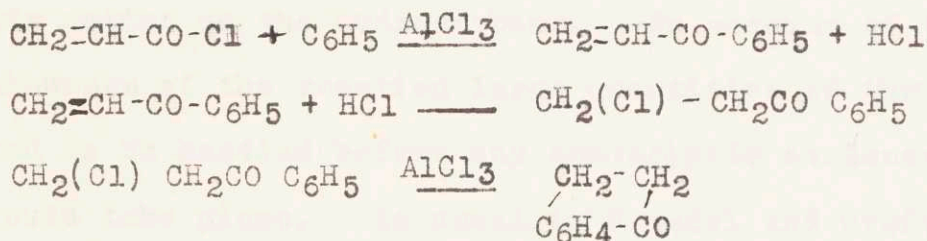
Propenylphenyl ketone: Crotonic acid was treated with bromine and from the resulting dibrom acid by a similar procedure as above propenyl phenyl ketone was obtained. It was a colorless liquid of boiling point 135 at 20 mm. It formed a compound with phenyl hydrazine which melted at 108° and which gave a green fluorescence in alcoholic solution.

Isobutenyl phenyl ketone: Dimethyl crotonic acid was the starting point in this case and by the same process as above, the isobutenyl phenyl ketone was obtained. The boiling point of this liquid ketone was 148 at 18 mm. The phenyl hydrazone had melting point 88°.

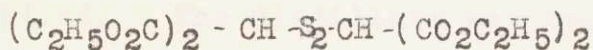
It is interesting that vinyl phenyl ketone has been prepared by still another method. H. Schaefer and B. Tollens¹ tried to make trimethylol acetophenone from formaldehyde and acetophenone. One of their products was trimethylol di acetophenone which upon being distilled with steam broke down to monomethylol-acetophenone. This in turn lost water and formed vinyl phenyl ketone. The authors found it to be a yellow oil with pungent odor, whose phenylhydrazone melted at 152° - 153° and produced fluorescence in solution.

¹.B. 36. 13555 (1903)
B. 39. 2187 (1906)

Moureu¹ tried to prepare vinyl phenyl ketone by the action of chloride of acrylic acid upon benzene in the presence of aluminium chloride. He obtained a crystalline product with melting point 42°, which was volatile with steam and was easily soluble in alcohol and ether. He prepared a phenyl hydrazine derivative which crystallized in yellow needles and melted at 130°. E. P. Kohler repeated the experiments of Moureu and proved that the solid obtained was not vinyl phenyl ketone but α hydrindone which was formed according to the following equations.



Friedel and Craft condensation has also been tried in the case of malonic ester. Wolff Ott² using sulphur chloride and malonic ester in presence of aluminium chloride obtained a compound of the formula:



1. Monreu. Ann.chim.Phys.(7) 2 198.
2. B.36.3725 (1903)

Experimental Details.

The condensation of the hydrocarbons with benzoyl chloride was effected by first preparing the compound of the latter with aluminium chloride in the presence of carbon disulphide and passing the gas at room temperature slowly through the mass of crystals covered with the solvent. The gas was dried by passing through a train of calcium chloride towers. Concentrated sulphuric acid had to be avoided because of its action on the hydrocarbons. On account of the slowness of the reaction large quantities of the gases had to be handled before any appreciable condensation could take place. As usual in Friedel and Craft condensations, the reaction product was treated with acidulated ice-water and the carbon disulphide layer was separated, washed and dried over calcium chloride. The solvent was then removed and the residue was steam distilled. The distillate was treated with sodium carbonate and was extracted with ether and dried over calcium chloride. The solvent was removed and the residual oil was carefully distilled under reduced pressure. Later on during the investigation it was

thought better to avoid steam distillation. But some method had to be used for the removal of the residual benzoyl chloride. In order to effect this, the reaction product contained in carbon disulphide solution was treated with an aqueous solution of sodium carbonate and was vigorously stirred for several hours by a mechanical stirrer. The carbon disulphide layer was separated and the rest of the procedure was the same as before.

For purification of the liquids a fractionating column was employed. Special adapters and pressure regulators were used during distillation under reduced pressure.

The phenyl hydrazine derivatives were prepared according to the method used by Kohler. About 3 gms of the Ketone and an equivalent quantity of phenyl hydrazine were added to 10 cc of alcohol containing a few drops of glacial acetic acid. The mixture was warmed on a water bath for about half an hour and on cooling, the crystals of the derivative were obtained. These were further recrystallized from alcohol until a constant melting point was reached.

Ethylene.

In order to satisfactorily identify the reaction products and study the most advantageous conditions for their formation several condensations had to be carried out. The conditions of the experiment were altered in various ways. The yields of the product were greater when the molecular compound $C_6H_5CO Cl$ $AlCl_3$ was used than when the reagents were all put together. It was also found that the ethylene was absorbed more easily when the reaction was carried out at the room temperature than at higher temperatures. The agitation of the mixture on a mechanical shaking apparatus helped the rate of absorption by offering a greater surface to the gas.

In experiments 1 and 2 the molecular compound of benzoyl chloride and aluminium chloride was prepared by boiling 20 gms of benzoyl chloride, 25 gms of aluminium chloride and 350 cc of carbon disulphide for 3 hours under a reflux condenser, and cooling the clear solution overnight. About 10 litres of dry ethylene were passed through this compound during 10 hours. A heavy oil was formed at the bottom of the flask and all the crystals

of the molecular compound disappeared. The product was subjected to the general process described above. A yellow oil was obtained which when distilled under reduced pressure (20 mm) boiled between the ranges 115° - 130°. While the first experiment was carried out we were looking for a solid, as Moureu had described vinyl phenyl ketone to be a solid of melting point 42° giving a phenyl hydrazone of m.p. 130°. We failed to get anything but the yellow oil. As Tollens described the ketone to be a yellow oil and stated the phenyl hydrazone to melt at 152° - 153° we performed the second experiment with the idea of verifying his results. About 0.5 gms of the yellow oil were treated with 0.5 gms of phenylhydrazine and 5 cc of alcohol, and the mixture was warmed for half an hour on a water bath. On cooling the solution, needle shaped crystals of the phenyl hydrazone were obtained with a melting point 146°. This was 16° higher than the phenyl hydrazone described by Moureu and 6° lower than that of Tollens. Experiments 3 and 4 were conducted with the idea of determining the percentage yield of the product and of obtaining quantitative data on the amount of gas absorbed. In the initial part of the 3rd experiment the temperature

of the mixture was raised to about 60° and it was found that this was retarding the absorption of the gas. The remainder of the experiment was carried out at the room temperature. During the course of treating the reaction product it was found that when the distillate from steam distillation was made neutral with alkali and kept over night, a small bunch of very fine crystals were found suspended in the aqueous layer in addition to the yellow oil. The solid was soluble in ether and was recrystallized. The crystals melted sharply at 105° and burnt on ignition with a smoky flame leaving no residue. About 3 gms of solid were produced and further tests were made on this as shown below.

The quantities of the reagents used and the products obtained are tabulated below.

Benzoyl chloride	30 gms
Aluminium chloride	30 gms
Carbon disulphide	400 cc
Ethylene passed through	20 litres
Ethylene absorbed	14 litres
Weight of the yellow oil	5 gms
% yield based on benzoyl chloride	17.5
% yield based on ethylene	21

Properties of the oil: The liquid boiled at 115° under a pressure of 20 mm. It gave a phenyl hydrazone which melted at 151° on two crystallizations. It possessed a piercing odor and was highly unsaturated as shown by the action upon bromine. The oil which was pale yellow when fresh turned darker on standing. This made us suspect the presence of halogen in it. By the color test on copper wire it was found to contain chlorine. The chlorine was estimated by treating the oil with 10% alcoholic potash and adding silver nitrate to the aqueous solution acidified with nitric acid. 4.86 gms of the oil gave 1.48 gms of silver chloride and this corresponds to 10.9 gms chlorine per mole of the vinyl phenyl ketone.* The properties of the ketone we obtained closely agree with those given by Tollens as well as by Kohler. The melting point of our phenyl hydrazone however is closer to the value of Tollens than that of Kohler.

The presence of chlorine in the oil seemed to change our point of view as regards the mechanism of the condensation. Hence, we prepared the hydrogen chloride addition product and studied its properties. By saturating the yellow oil in ether solution with dry

* This shows that 30% of the crude product is the compound containing chlorine.

hydrogen chloride a solid was obtained which crystallized in plates melting at 51° , about 6° lower than the value given by Kohler for β chlorpropiofenone. The crystals were insoluble in alkali and were easily volatile with steam. Kohler found that this solid in presence of aluminium chloride easily changed over into α Hydrindone. This fact is very interesting. If the reaction between ethylene and benzoyl chloride was one of addition, the resulting β chlorpropiofenone would change over completely to α hydrindone and no vinyl phenyl ketone would be formed. On the other hand if the hydrogen activated by the double bond were replaced by the benzoyl group there would be very little chance for the formation of hydrindon. In our experiment we obtained neither α hydrindone nor β chlorpropiofenone among the products of condensation and therefore the first hypothesis is improbable.

Properties of the solid by product: It crystallized in needle shaped crystals, melting at 105° possessed no unsaturation. Its molecular weight, determined by the freezing point method using benzene as solvent was 268.

0219	gms	of	solid	lowered	freezing	point	of		
					16.33	gms	benzene	by	0.45°
3086	"	"	solid	lowered	freezing	point	of		
					14.77	gms	benzene	by	0.37°

On analysis it was found to possess the following composition.

0.1599 gms of solid gave .4320 gms CO₂ and .0927 gms H₂O
0.1160 " " " " .3149 gms CO₂ and .0674 gms. "

	I.	II.	Average
C.	73.66	74.01	73.83
H.	6.44	6.46	6.45

The solid dissolved in concentrated sulphuric acid to a brown solution and was reprecipitated on dilution. But we could not confirm the presence of ketonic group for neither phenyl hydrazine nor hydroxylamine gave any derivatives.

Propylene.

As in the previous experiments the propylene was passed through the molecular compound $C_6H_5CO Cl AlCl_3$ in carbon disulphide at room temperature. Out of 6.5 litres that were passed through about 5 litres were absorbed. After the usual procedure of decomposition with water, steam distillation, etc. 13 gms of a clear liquid were obtained boiling at $134^\circ - 136^\circ$ under reduced pressure (20 mm).

Wt. of benzoyl chloride	20 gms
Wt. of aluminium chloride	24 gms
Propylene absorbed	5 litres
Wt. of product	13 gms.
Yield of Ketone based on benzoyl chloride	62 %
" " " " " propylene "	39 %

In a second experiment we tried to find if propylene itself formed a compound with $AlCl_3$ in CS_2 , but obtained negative results. It was also found that the yield of the ketone was small when the mixture of the reagents was employed instead of the molecular compound. Thus 20 gms benzoyl chloride 25 gms aluminium chloride, and 10 litres of propylene, yielded only 4 gms of ketone.

Properties: The liquid boiled at 134° - 136° at 20 mm and was highly unsaturated. The copper wire test showed the presence of chlorine. The chlorine was quantitatively estimated. • 3169 gms of the liquid gave .623 gms of silver chloride. That is 6.4 gms chlorine per mole of the propenyl phenyl ketone.* In order to understand the condensation better we tried to prepare the hydrochlor addition product by saturating the liquid with dry hydrogen chloride. A deep red liquid was obtained which on being treated with dilute alkali or on steam distillation produced the original unsaturated ketone. The dibrom compound was a solid, crystallizing in needles, and not affected by dilute alkali. Its melting point was 102°. The phenyl hydrazone came out in yellow plates of melting point 108°, which agrees with Kohler's values.

* This shows that 17% of the product is the compound containing chlorine.

Isobutylene.

Dry isobutylene was passed through the molecular compound of benzoyl chloride and aluminium chloride. The reaction product gave a deep purple color to the solvent. By the usual method the product was purified. When distilled under reduced pressure 19 mm two fractions were obtained.

Fraction I. 130° - 132° 3 gms.

Fraction II 135° - 148° 10 gms.

Wt. of benzoyl chloride 25 gms.

Wt. of aluminium chloride 25 gms.

Isobutylene passed 10 litres.

Yield of product 13 gms.

The second fraction was redistilled at 18 mm and the boiling point was 139° - 142°. The usual test for chlorine was applied and it was found to be present. The phenyl hydrazone reaction gave a white crystalline derivative which easily turned dark on exposure to air and which melted at 86° 87°, which is in agreement with Kohler's determination.

The yield of the product based on benzoyl chloride was 45.5 %.

Normal butylene.

In this experiment 20 gms of benzoyl chloride and 25 gms of aluminium chloride were used. The reaction product after the passage of normal butylene was deeply colored. The final product when distilled under reduced pressure gave two fractions. Thus at 14 mm the fraction I boiled at 115° - 120°, and the fraction II boiled at 125° - 135°. The yield was 8 gms in I and 11 gms in II, the total amounting to 19 gms. The yield based on benzoyl chloride was 83 %. Both the fractions contained chlorine. The phenyl hydrazone was prepared and it melted at 130° - 131°. By treatment with 10% alcoholic potash the amount of chlorine in the ketone was determined. 17.36 gms of the crude product gave 3.91 gms of silver chloride, i.e. 9.44 gms chlorine per mol of the unsaturated ketone.*

The product obtained after treatment with alcoholic potash gave two fractions again. The first boiled at 99° - 102° at 5 mm and the second at 115° - 122° at 5 mm. Equal quantities of both were produced. As this ketone was not described in the literature, an analysis was made on both the fractions separately.

*This shows that 26 % of the product is the compound containing chlorine.

Fraction	Wt. of Sample	CO ₂	H ₂ O	% C	% H
I	.2036	.6079	.1699	81.5	9.25
I	.1995	.5951	.1667	81.33	9.28
I					
II	.2358	.6982	.1837	80.73	8.66

This discrepancy between fraction I and II was thought to be due to the presence of the ether $\text{CH}_3\text{-CH}_2\text{-CH}(\text{CH}_3)\text{-CH}_2\text{-CO C}_6\text{H}_5$

The % values of normal butenyl phenyl ketone would be
C 82.5% H 7.5%

The % values for the ether $\text{CH}_3\text{-CH}_2\text{-CH}(\text{CH}_3)\text{-CH}_2\text{-CO C}_6\text{H}_5$

would be C 75.0 H 8.33

Further investigation is necessary before we can account for the lack of agreement between the theoretical values and those actually found.

Trimethyl ethylene.

A mixture of 20 gms benzoyl chloride and 20 gms of aluminium chloride and 400 cc carbon disulphide was used for the preparation of the molecular compound. This compound was placed in a flask fitted with a reflux condenser and 10 gms of trimethyl ethylene were added and the mixture was left standing overnight. The crystals of the compound disappeared and a layer of heavy oil was formed at the bottom of the flask. After 24 hours the solvent was removed and the usual procedure was applied. When distilled under reduced pressure 13 mm three fractions were obtained

Frn.	B.P.	Vol.	Total Wt.	Yield based on trimethyl ethylene was
I	120 - 125	10 cc	18 gms	72.4% Yield based on benzoyl chloride was 72.4%
II	130 - 140	4 cc		
III	140 - 160	3 cc		

The three fractions were colorless first, but turned greenish on standing. We tested them for halogens. There was chlorine in each of the fractions. The phenyl hydrazone of the compound was prepared and it melted at 90° - 92° and it contained chlorine.

gms of trimethyl ethylene.

* This shows that 5.2% of the product is the material containing chlorine.

The 3 fractions together were treated with 10 % alcoholic potash on a warm bath for half an hour. The mixture was poured into water and the oily layer was extracted with ether and redistilled under reduced pressure. Three fractions were obtained. The boiling points were as follows at 13 mm:

Fraction I	had	boiling	point	115° - 120°
Fraction II	"	"	"	125° - 130°
Fraction III	"	"	"	140° - 150°.

The yields of the three fractions were : 5 gms, 5.5 gms, and 1.5 gms respectively. Total 12 gms. The yield calculated after the alcoholic potash treatment was 48%. The chlorine content was estimated. 11.88 gms of product gave .068 gms of silver chloride. One mole of unsaturated ketone has .25 gms chlorine. * The phenyl hydrazones of the new fractions I and II were prepared separately and each had a melting point 127°. The two were mixed and the melting point was 127°. This showed the presence of the ketone in each fraction.

The fractions I and II were mixed and were saturated with dry hydrogen chloride. The liquid turned deep blue. It boiled between 135° and 140° at 13 mm. Therefore a second batch of the ketone was prepared using 25 gms of benzoyl chloride, 30 gms of aluminium chloride, and 20 gms of trimethyl ethylene.

* This shows that 0.8 % of the product is the compound containing chlorine.

The crude product gave two fractions. The first boiled between 137° - 142° and the second between 145° - 165° at 14 mm. The yield of the first fraction was 7 gms. and of the second 5 gms. Both contained chlorine. After the alcoholic potash treatment two fractions were again obtained. The first fraction boiled at 118° - 125° and the second at 130° - 140° at 5 mm. The yield of the first was 5 gms and of the second 4 gms. Total 9 gms. In order to obtain very pure samples for analysis the two fractions were again distilled with a fractionating column. At 11 mm the fraction I boiled between 128° - 132° and the fraction II boiled between 135°-145°.

Analysis:

Fraction	Wt. of Sample	CO ₂	H ₂ O	C	H
I	.2134	.6472	.1655	82.7	8.62
I	.2509	.7613	.1920	82.7	8.50
II	.2170	.6558	.1816	71.29	9.29

The theoretical values for the ketone $(CH_3)_2C=O \cdot CO \cdot C_6H_5$ would be C 82.78 H 8.05

The value for the ether $(CH_3)_2C(OCH_3)-CO-C_6H_5$ would be C 75.72 H 8.74.

Phenyl ethylene

The purpose of this experiment was to find how the phenyl group would affect the condensation when a phenyl substituted ethylene was employed. The benzoyl chloride aluminium chloride compound was first prepared and placed in a flask fitted with a reflux condenser. Phenyl ethylene was added slowly. It was found that immediately the hydrocarbon came in contact with the compound there was a kind of heavy gum formed and the carbon disulphide layer became very clear. This mixture was, however, warmed on a water bath for a few hours and the usual decomposition with water and steam distillation was carried out. It was found that no product could be isolated and only ^ahard gummy mass was left at the bottom of the flask. We suspected here that phenyl ethylene may have undergone polymerization in presence of aluminium chloride. On reference to the literature¹ it was found that phenyl ethylene forms a compound $\text{AlCl}_3 \text{C}_6\text{H}_5\text{-CH}=\text{CH}_2$ with aluminium chloride. Hence our experiments to carry on the condensation failed to give any results. If the condensation were successful, we should have obtained the compound benzylidenacetophenon² $\text{C}_6\text{H}_5\text{-CH}=\text{CH-CO-C}_6\text{H}_5$ which melts at $57^\circ - 58^\circ$, and boils undecomposed at

¹.J.A.C.S.39, 1422. (1917)

².Beilsbein, page 246;

345° - 348°. Its oxime would be $C_6H_5 CH C C_6H_5$
NOH
which melts at 107° - 108°.

Diisopropyl.

As in the previous case, the molecular compound was prepared using 20 gms benzoyl chloride, 25 gms aluminium chloride and 150 cc carbon bisulphide. This was placed in a flask fitted with a reflux condenser and placed in an ice bath. About 10 gms of diisopropyl were gradually added into the flask. There seemed to be vigorous reaction and the mixture warmed up. The mixture was let stand for 24 hours at room temperature and then warmed on a water bath for 6 hours. There was a layer of oil at the bottom and the crystals had disappeared. This was decomposed with ice water and the carbon disulphide layer was separated and treated with an aqueous solution of sodium carbonate. The mixture was vigorously stirred by means of a high speed stirrer. After four hours the emulsion was allowed to settle and again the carbon disulphide layer was separated and washed and dried. After removal of the solvent the residue was distilled under reduced pressure. Two fractions came off at 11 mm pressure.

Frn.	B.P.
I	107° - 112°
II	120° - 130°

This does not agree at all with the compound Isopropyl dimethyl acetophenone¹ which we expected in the reaction. The ketone is described as a liquid boiling between 120 - 126 at 11 mm and its oxime is a solid melting 152°- 153°. It was prepared by the action of isopropyl iodide upon the sodium compound of dimethyl acetophenone $C_6H_5-CO-CH(CH_3)_2$. An analysis was made for the determination of the percentage of carbon and hydrogen

Frn.	Wt. of Sample	CO ₂	H ₂ O	C	H
I	.2120	.5708	.1358	76.02	7.12
I	.2002	.5610	.1359	76.4	7.54
II	.3001	.8059	.1940	73.3	7.2

The percentages in the isopropyl dimethyl acetophenone would be C 82.1; H 9.47

The dibenzoyl compound $(CH_3)_2C(=O)C_6H_5$ — $C(=O)C_6H_5$ would

have C 81.6 H 7.48.

Hence, our compound could not be the ketone sought for

¹. A. Haller and E. Bauer Ann. de Chim et de phys.

Malonic ester (ethyl malonate)

The fact that the hydrogen in malonic ester is easily replaced by a nitro group led Professor Norris to suggest the application of Friedel and Craft reaction to this substance.

Using 22 gm benzoyl chloride, 20 gms aluminium chloride and 300 cc carbon disulphide the molecular compound was prepared and placed in a flask fitted with a reflux condenser. 25 gms malonic ester were added. Soon after the addition, heat was produced and a white, sticky compound sank to the bottom of the flask leaving the carbon disulphide layer clear. On refluxing for six hours the sticky mass turned brown and grew more viscous. The reaction product was decomposed with water and after the solvent was removed the residue was distilled under reduced pressure (13 mm). The distillate consisted mostly of unchanged benzoyl chloride and malonic ester and a small quantity of brown oil which boiled about 140°-160°. This led us to suspect that malonic ester itself had formed a compound with aluminium chloride and came off on distillation. In order to test this a blank experiment was made with six gms malonic ester, 12 gms

aluminium chloride and 100 cc carbon disulphide. The mixture was left standing for a week. The aluminium chloride became covered with a brown gummy mass. The carbon disulphide was decanted off and distilled. There was no trace of malonic ester in it. The gummy mass was transferred into a distilling flask and distillation was carried on at 13 mm. Malonic ester came off the gummy layer. About 2 gms were recovered: This proved that malonic ester formed a compound with aluminium chloride.

A search was made into the literature to see if any work was done on this subject. Walker and Spencer¹ had worked on the action of aluminium chloride on malonic ester and obtained the molecular compound $\text{H}_2\text{C}(\text{COOC}_2\text{H}_5)_2 \text{AlCl}_3$. It was also found in the literature that malonic ester had been previously used in Friedel and Craft condensation. Wolf and Ott² had succeeded in obtaining the compound $(\text{COOC}_2\text{H}_5)_2 \text{CH-S-S-CH}-(\text{COO C}_2\text{H}_5)_2$ by the action of S_2Cl_2 on malonic ester in presence of aluminium chloride.

Therefore another experiment was made using

¹. Soc. 85 1108
Am. Ch. J. 24 385 (1901)
². B. 36 3722 (1903).

21 gms benzoyl chloride, 20 gms aluminium chloride and 27 gms malonic ester, all mixed together in a flask fitted with a reflux condenser and warmed on a water bath for 6 hours. A hard horny mass was produced. This was decomposed with water and the mixture was extracted with ether and redistilled at 13 mm. Three fractions came off.

Fraction	B.P.	Volume
I	95°-105°	5 cc
II	140° - 150°	20 cc
III	180° - 190°	3 cc

Fraction I was perhaps unchanged malonic ester. The Fraction II was treated with sodium bicarbonate solution and extracted with ether. On redistillation a liquid was obtained which boiled at 160° at 13 mm.

If the condensation had proceeded as we expected it to do, we should have obtained the compound benzoyl malonic acid ether¹, $C_6H_5-\underset{\substack{| \\ OH}}{C} = C-(COO C_2H_5)_2$ The properties have been described thus: It is a yellow oil of boiling point 192° - 193° at 13 mm. It is a

1. Ann der chem 281-282 (1894)

strong acid, soluble in sodium carbonate solution and is liberated unchanged by mineral acids. With ferric chloride it gives red color in alcohol solution. On distillation with steam it yields benzoyl acetic acid and alcohol. With cupric acetate it gives dark green crystals from alcohol melting at 180°.

The liquid obtained in our experiment was **not** soluble in sodium carbonate. It could not be ethyl benzoate for it gave a yellow oil even on refluxing with sodium hydroxide. The liquid, however, gives a deep red color when treated with ferric chloride in alcoholic solution.

Acetone.

A condensation was attempted using acetone and the molecular compound $C_6H_5CO Cl AlCl_3$. It was found that no reaction took place at all. A small quantity of a solid product however was found which was soluble in alcohol and gave a deep purple color to it. It did not melt sharp. Benzoyl acetone¹ itself is a solid of melting point 60 - 61. It boils undecomposed at 260° - 262°. It is difficultly soluble in cold water, very easily in alcohol and ether, easily soluble in sodium hydroxide, difficultly in sodium carbonate and not in sodium bicarbonate. With ferric chloride it gives an intense red color.

1. Clausen Lowman B. 21 1150 (1888)

Preparation of the reagents.

The unsaturated hydrocarbons were all obtained by dehydrating the corresponding alcohols. But different methods were employed for dehydration as shown below.

1. By the use of phosphorus pentoxide¹
2. By the hot tube method with aluminium²
oxide as catalyst.
3. By the use of sulphuric acid (1:2).³

The first method was applied for the preparation of ethylene, propylene and normal butylene. The calculated amount of phosphorus pentoxide was placed in the bottom of a distilling flask with the side tube stoppered and with a reflux condenser. The flask was kept in an ice bath and the corresponding weight of alcohol was poured through the condenser tube, very gradually taking care to prevent loss of material by overheating. After all the alcohol was added, the flask was taken out of the ice bath and was warmed until all the phosphorus pentoxide had gone into solution. The reflux condenser was then removed and the flask was connected to the gas holder. The bottom of the flask was heated gently with a small flame. The hydrocarbon was evolved steadily.

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1. Practical org.chem.J.F.Norris.
 2. B.36 1997 (1903)
 3. J.M.Joubert.M.I.T.Ph.D.Thesis 1922.

The results are tabulated below.

Hydrocarbon	Alcohol	Wt. of Alcohol	Wt. of P ₂ O ₅	Vol. of Hydro-carbon	% Yield.
Ethylene	Ethyl Alcohol	30 gm.	40 gm.	12 litres,	82%
Propylene	Isopropyl Alcohol	21 gm.	10 gm.	5 litres,	70%
N-butylene	N.butyl Alcohol.	30 gm.	20 gm.	6 litres,	66%

The second method was applied for isobutylene. A big sized test tube of silica was fitted with a rubber stopper having two holes. Through one of these was passed the stem of a dropping funnel for the alcohol, and through the other a tube which was bent at right angles and was connected to a long silica tube enclosed in an electric furnace. Inside this furnace tube was placed dry aluminium oxide which served as a catalyst. The temperature of the furnace was measured by a calibrated thermo-couple and kept around 400° by regulating the electric current through the furnace coils. An oil bath was placed under the vertical silica tube and heated up to about 200°. The isobutyl alcohol was gradually let into the silica tube from the dropping funnel. The alcohol was vaporized

and on passing over the hot catalyst was converted into isobutylene. The method was very satisfactory.

Results of Experiment.

Wt. of isobutyl alcohol	30 gms
Volume of isobutylene	8 litres
% Yield	88%

The third method was applied for the preparation of trimethyl ethylene. On account of the great tendency of this hydrocarbon to polymerize on coming in contact with phosphorus pentoxide or concentrated sulphuric acid, a suitable dehydrating agent was necessary to prepare it from tertiary amyl alcohol. Mr. J.M.Joubert who is investigating the polymerization of the different unsaturated hydrocarbons in our laboratory has found that sulphuric acid of strength 1:2 is very suitable for the preparation of trimethyl ethylene. The required quantity of the well-cooled tertiary amyl alcohol was mixed with the calculated amount of (1:2) sulphuric acid in a distilling flask and the mixture after a good shaking was heated on a water bath. The trimethyl ethylene separated out as the upper layer on the acid and was easily distilled off. The crude distillate was dried

first over calcium chloride and then over sodium and finally was redistilled carefully. The pure hydrocarbon came off between the temperature 38° 40°. The results are shown below:

Wt. of tertiary amyl alcohol	30 gms.
Vol. of 1:2 sulphuric acid	72 gms.
Wt. of trimethyl ethylene	20 gms.
% Yield	80 %

Preparation of styrol.(phenyl ethylene).

Cinnamic acid dissolved in glacial acetic acid was saturated with dry hydrogen bromide and crystals of hydrobrom cinnamic acid were obtained. This substance was treated in the cold with an aqueous solution of sodium carbonate. Carbon dioxide was evolved and an oil with an etherical odor separated out. This was extracted with ether, was dried over calcium chloride and was distilled after the removal of the solvent. Liquid boiling at 144° was collected. The hydrogen bromide used in this experiment was prepared by dropping bromine into benzene containing few clean pieces of iron. The evolved gas was further freed from bromine vapors by passing through a column of anthracene.

Wt. of cinnamic acid 50 gms.

Wt. of hydrobrom cinnamic acid obtained 90 gms.

Wt. of phenyl ethylene 30 gms.

% Yield, 37 %

Preparation of diisopropyl. Apparently an easy method to obtain this hydrocarbon would be the Wurtz synthesis. Schorlemer¹ treated isopropyl iodide with sodium in presence of dry ether and obtained diisopropyl. His yield was very poor. In our laboratory the method was modified and only dry isopropyl iodide and sodium were used. Freshly distilled isopropyl iodide reacted quickly with clean sodium in the shape of thin shavings. A blue crust was formed on sodium, and the mixture was left over night for the completion of the reaction. By careful distillation a low boiling liquid (60°-70°) was obtained which on further treatment with sodium yielded a liquid boiling about 60°-63°. This was found to contain traces of isopropyl iodide. Hence the crude product was treated with concentrated sulphuric acid and strong nitric acid using a reflux condenser and an ice bath to regulate the heat of reaction.

1. A. 144 184
 214 167
 301 179

B. 31 1801 (1898)
 Soc.77 1131
 C. (1899) I,1065.

The traces of isopropyl iodide were completely eliminated and the pure diisopropyl was distilled off by the use of a fractionating column and a suitable condenser.

The boiling point of the diisopropyl was 58°.

Wt. of isopropyl iodide 190 gms.

Wt. of diisopropyl 10 gms.

% Yield. 10.5 %

It is an interesting fact that this synthesis does not give a good yield, if the isopropyl iodide has been allowed to stand for more than a few hours. The acceleration of the reaction when the freshly distilled isopropyl iodide is employed could not be ascribed to the presence of free iodine, because the addition of crystals of iodine did not improve the yield in the second case. Magnesium was tried in place of sodium, but did not give any diisopropyl at all. When magnesium and ether were employed, only the Grignard compound was formed.

Preparation of aluminium chloride.¹

Pure anhydrous

aluminium chloride was prepared by passing dry hydrogen chloride over aluminium ribbon placed in a hot glass tube. The aluminium was first heated moderately and when the hydrogen chloride began to react with it, the heat produced was sufficient to continue the process with a small flame. The pure aluminium chloride sublimed and was collected in a bottle attached to the long tube. It was found necessary to have a very rapid current of hydrogen chloride through the apparatus, so as to avoid blocking the cooler end of the tube.

Wt. of aluminium

Wt. of aluminium chloride

% Yield, 69%

1. Gattermann. Pr. Methods in Org.Chem. page 386.

APPENDIX.

Born in Bangalore, India, 1893. Primary and secondary education in the local school. Joined the University of Madras in 1909 and obtained the degree of M.A. (Hons.) in 1916. Worked as a post graduate scholar in the Department of Electro Technology, Indian Institute of Science, Bangalore, until March 1919, and obtained the diploma of Associate of the Institute. Entered the Massachusetts Institute of Technology in October, 1919 and took up graduate work in the Department of Chemistry. During the summer of 1917 worked as a student apprentice in the Tata Iron and Steel Co., Jamshedpur, India and in the summer of 1918, worked as apprentice in the Steam Power Plant at Hyderabad and the hydroelectric plant at Sivasamudram. In the summer of 1921, the School of Chem. Eng. Practice, M. I. T. kindly permitted me to work as a special student at their Station in the Eastern Mfg. Co., Bangor, Maine.
