

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report
of
Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Elwin Elmer Harris for the degree of Master of Science. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science.

Bob Frankforter
Chairman

Lee Irwin Smith

F. H. MacDugall

Date _____

THE UNIVERSITY OF MINNESOTA
GRADUATE SCHOOL

Report
of
Committee on Examination

This is to certify that we the undersigned, as a committee of the Graduate School, have given Elwin Elmer Harris final oral examination for the degree of
Master of Science.

We recommend that the degree of
Master of Science
be conferred upon the candidate.

G. B. Frankforter
Chairman

J. H. MacDougal

Lee Irwin Smith

W. A. Hunter

M. C. Sneed

Date _____

A COMPARISON OF ALUMINIUM CHLORIDE AND FERRIC CHLORIDE
THE ACTION OF BROMAL ON PHENOLIC ETHERS IN THE PRESENCE
OF ALUMINIUM CHLORIDE AND FERRIC CHLORIDE

A THESIS

SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF MINNESOTA

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE

MASTER OF SCIENCE

(Department of Chemistry)

By

Elwin Elmer Harris

November 1922

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A COMPARISON OF ALUMINIUM CHLORIDE AND FERRIC CHLORIDE

Historical Part

Part 1.

As condensing agents by splitting out hydrogen chloride

It has long been known that ferric chloride and aluminium chloride have similar actions as condensing agents. Anhydrous ferric chloride is used in much the same way as anhydrous aluminium chloride except that the reactions are not so violent as those of aluminium chloride and for that reason ferric chloride may be used in many cases where aluminium chloride cannot be used. When aluminium chloride is used, yields are much greater than when ferric chloride is used, but the yields with the latter are smaller in most cases where they can be used in the same reaction.

Boesekin¹ obtained ferric chloride combination compounds corresponding to those that Gustavson² obtained in reactions with aluminium chloride and similar to those obtained by Perrier³ in explaining the preparation of a ketone by the aluminium chloride method. Boesekin introduced 2.8 grams of benzoyl chloride and

1. Ann. 217 243
2. J. P. Ch. 2, 68, 209
3. Cr. 116, 1300

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1.8 grams of ferric chloride into a flask containing 100 cc. of carbon disulphide and boiled the mixture until it became a clear brown liquid. When it cooled, crystals formed having the composition corresponding to $C_6H_5COCl.FeCl_3$. These, like the aluminium chloride addition compound obtained by Gustavson, were very hygroscopic and decomposed on exposure to the atmosphere. The dark crystals yield, on boiling with benzene, crystals of the composition $C_6H_5COC_6H_5.FeCl_3$. Ferric chloride gives the same product as aluminium chloride except that the yields are lower and for ordinary purposes it does not find as wide an application.

After a study of the work that had been completed on ferric chloride Nenki⁴ raised the question as to the difference, if any, between ferric chloride and aluminium chloride. He found that an acyl- or alkyl-radical can be introduced into the benzene ring of a mono-hydroxy-phenol as the mono-substitution product, as is the case with aluminium chloride, but he discovered a difference between the di- and tri-hydroxy-phenols which form some of the di-substitution product as well as the mono-substitution product.

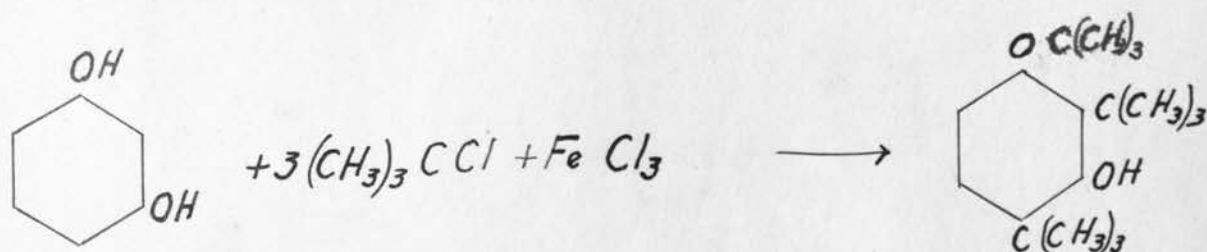
According to Friedal and Crafts⁵ the aluminium chloride does yield the di- and tri- when an excess of phenol is present. With ferric chloride there results from phloroglucin and acetylchloride a diketone of the formula $C_6H_2(COCH_3)_2(OH)_3$, also the mono ketone $C_6H_2(COCH_3)(OH)_3$. Since these have the same percentage composition,

4. Ber 32. 2417

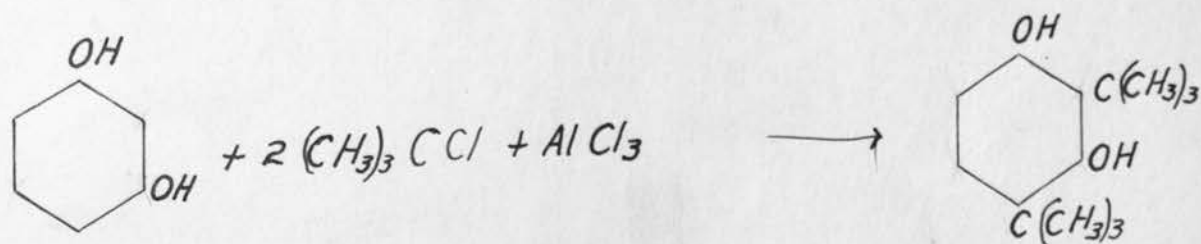
5. Be. Mar 29, 2

they may be distinguished from each other only by the determination of the molecular weight. If twice the amount of ferric chloride and four times the amount of acetyl chloride is used, one still obtains a mixture of the mono-acetyl and diacetyl phloroglucin.

A peculiarity of the synthesis formed with ferric chloride ⁶ is that in the action of organic halides on the phenols, not only is substitution made for the hydrogen on the ring, but also on the hydroxyl of the phenols. As in the case of tertiarybutylchloride on resorcin, the butyl ether of dibutylresorcin resorcin is produced.



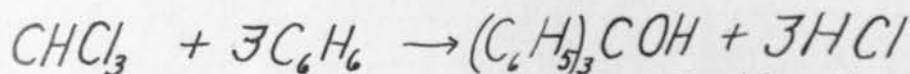
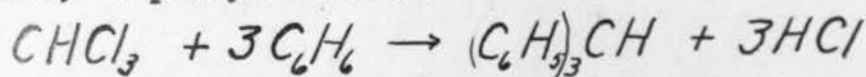
on the other hand, with aluminium chloride one gets only the dibutylresorcin.



6. Ber. 32, 1716

But of the butylchlorides only the tertiarybutylchloride acted in this way as no such substituted products resulted from the normal and secondary butylchloride, in which cases the action is the same as when aluminium chloride is used.

In the synthesis with ferric chloride there is also chlorination and oxidation. From chloroform and benzene one obtains, besides the triphenyl-chlormethane, some of the oxidized product, triphenyl carbinol.



From acetylchloride and *m*-xylene besides the dimethylacetophenone some of the ortho-para-xylalacetyl is formed.

The butylchloride and hydroquinone give the dibutyl quinone and no dibutylhydroquinone. The ferric chloride acts as an oxidizing as well as a condensing agent.

Meissel ⁷ obtained from carbon tetrachloride and benzene 75% of the theoretical yield of triphenylchlormethane while Gomberg ⁸ with aluminium chloride obtained a yield of 90% of the theoretical yield.

Senkowski ⁹ in working with different temperatures found that better yields were obtained from either aluminium chloride

7.	Ber.	32,	1716
8.	Ber.	33,	3144
9.	Ber.	23,	2413

or ferric chloride if the temperature was kept low and the experiment extended over a longer time. In the reaction of isobutyl chloride and benzene at 4°C he obtained a yield of 70% of trimethyl-phenyl-methane while at $25^{\circ} - 30^{\circ}$ he obtained no trimethyl-phenyl-methane at all.

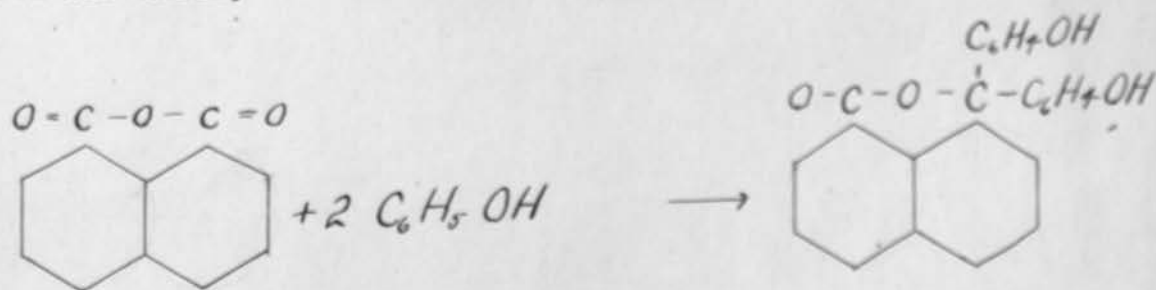


Part 2.

Dehydrating action of ferric chloride and aluminium chloride

(It is this action that will be dealt with in this paper)

Jaubert ¹⁰ found that 1-8 naphthol acid anhydride did not react with phenol in the presence of concentrated sulphuric, zinc chloride, or stannous chloride. However, when aluminium was used one easily obtains the phthalin.



10. Ber. 26, 992

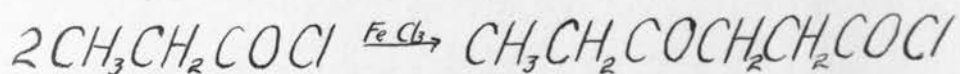
Nencki¹¹ found that in most cases as a condensing agent zinc chloride, by splitting out of water, gave much better yields than ferric chloride. One equivalent of acetic acid, one of phenol and one of ferric chloride gave a very small yield. Acid chlorides with phenols gives better yields than the corresponding alkylchlorides with phenols in contact with ferric chloride.

From hydroquinone and acetyl chloride Nencki¹² received only the ester $C_6H_4 (OCOCH_3)_2$ while with zinc chloride he received only the quinacetophenone. With aluminium chloride one receives the acetyl group attached to the ring with no change from the hydroquinone or a hydroquinoneacetophenone. With chloracetic acid and $POCl_3$ condensing with hydroquinone, he received the two products $C_6H_3 (COCH_2Cl) (OH)_2$ and $C_6H_2 (COCH_2Cl) (OH)_3$. In contact with ferric chloride, benzoyl chloride and benzene, a yield of about 70% of benzophenone is obtained. Acetyl chloride and phenol give about a 30% yield of $CH_3CO C_6H_4 OH$. Bralobrzieski¹³ and Nencki condensed acetyl chloride and salicylic acid in the presence of ferric chloride forming the acetylsalicylic acid, $C_6H_3 (CH_3CO) (OH) (COOH)$.

Hamonet¹⁴ discovered a peculiar reaction of ferric chloride

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|-----|------|------------|------|
| 11. | Ber. | 30, | 1777 |
| 12. | Ber. | 30, | 1777 |
| 13. | Ber. | 30 , | 1777 |
| 14. | Ber. | Par. 3, 2, | 334 |

that has not been accomplished with any other agent. He was able to prepare a ketone fatty acid from the action of ferric chloride on the acid chloride at low temperatures. For example, two molecules of propionic acid chloride is cooled down below zero and ferric chloride added in small portions at the time, until one equivalent to two of the acid chloride has been added. This is kept cool for some time, then warmed up to about 50 ° when one molecular weight of hydrogen chloride is given off for each two molecules of the acid chloride.



This is then cooled and covered with absolute alcohol. The action of the acid chloride on the alcohol is slow, but gradually the reaction mixture is taken up in the alcohol. This is then washed two or three times with water to remove the excess of alcohol, then dried over calcium chloride and distilled in fractions. A product representing about 15 - 20 % of the theoretical yield of $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{COOC}_2\text{H}_5$ is obtained, the ester being formed by the action of the acid chloride on the alcohol. The reactions of aluminium chloride as a dehydrating agent were discovered by Frankforter and Poppe (1912) in reactions with pinine, chloral, and aluminium chloride. These are very complicated if allowed to take place at room temperature, but at a low temperature only a molecule of water is split out.

In experiments with anisol and phenetol and chloral and aluminium chloride a simple reaction is obtained giving the trihalogen condensation product with these phenolic ethers.

Combes ¹⁵ using benzene, chloral and aluminium chloride obtained a very complex reaction from which he was able to isolate four different substances, diphenylchloralhydrochloride and dephenyldichlorethane melting at 74 °, tetraphenyl-ethane and an unknown compound melting at 83 °.

Blitz ¹⁶ using the same reagents obtained tetraphenylethane dichlorodiphenylethylene melting at 80°, triphenyl-~~v~~nylalcohol, $(C_6H_5)_2 C = C (OH) C_6H_5$ melting at 136° and also an unknown compound melting at 233°.

Later Boesekin ¹⁷ attempted the same reaction.

Drenesmann ¹⁸ obtained the following reaction:



or the simple alcohol condensation.

It will be seen that ferric chloride and aluminium chloride have similar reactions:

1. Ferric chloride gives better yields when the actions of aluminium chloride are violent.

15. Bull 45, 226

16. Ber. 26, 1952

17. Rec. Trav. Chem. 30, 381

18. Compt. Rend. 141, 201

2. Ferric Chloride has the property of oxidizing a compound as well as causing a condensation.

3. Ferric chloride in most actions gives much lower yields than aluminium chloride.

Experimental Part

A study of the action of ferric chloride with reference to different solvents, and the action on mixtures of bromal and phenetol.

It has been noted that when aluminium chloride is allowed to stand in alcohol a compound corresponding to a hydrate is formed with the alcohol. A similar compound was found in the case of ferric chloride and alcohol.

When ferric chloride is placed in a dry flask and a large excess of absolute alcohol is added and the mixture is allowed to stand for several weeks, and then cooled down by a freezing mixture a jelly like precipitate is formed. This is collected on a funnel cooled by a freezing mixture and suction is used to draw off the excess alcohol. No crystalline structure could be observed but an analysis gave the following percentages for iron, chlorine, carbon and hydrogen: oxygen being considered as the balance.

An analysis of the substance was as follows:

.9604 g	gave	.2131 g of Fe_2O_3	and	1.277 g	of Ag Cl
1.4190 g	gave	.3150 g of Fe_2O_3	and	1.8876 g	of Ag Cl
.2980 g	gave	.2843 g of CO_2	and	.1743 g	of H_2O
.3128 g	gave	.3016 g of CO_2	and	.1885 g	of H_2O
		I.	II.	III.	IV.
Fe		17.24%	17.26%		
Cl		32.90%	32.90%		
C				26.02%	26.30%
H				6.50%	6.70%
			10.		

This corresponds to the formula $\text{FeCl}_3 \cdot 3\frac{1}{2}(\text{C}_2\text{H}_5\text{OH})$ When this mixture was warmed, it seemed to go into solution, forming a greenish brown solution. On exposure to air it gradually took on moisture to become the hydrate. If this mass was heated as for distillation, a small amount of the ferric chloride distilled over with the alcohol till when almost all of the alcohol had been driven off and the temperature had been raised to about 170° , traces of ethyl chloride were noticed coming over with the alcohol.

Ether and ferric chloride were treated in the same way and a precipitate similar but darker in color was formed and was so unstable that no satisfactory analysis of the compound has yet been obtained.

Ferric Chloride does not react with pure dry carbon tetrachloride and is not very soluble in it. However, the partially hydrated form is soluble, giving a brown solution.

When ferric chloride is used in the regular Friedal Crafts action, the yields obtained were very low.

When methyl chloride is prepared and passed into boiling benzene for twelve hours in contact with anhydrous ferric chloride toluene is formed but only 30% of the theoretical yield is obtained, while those who use aluminium chloride report yields as high as 90% by this same method.

It has been found, however, that ferric chloride serves very well in the rôle of a dehydrating agent, as recently this substance has been used in the preparation of methylal from methyl

alcohol and trioxymethylene by splitting out water. Yields as high as 90% have been obtained.

The work of Frankforter and Kritchevsky¹⁹ was continued ferric chloride being used in place of the aluminium chloride used by them, with bromal and phenetol. Twelve grams of phenetol 14 grams of bromal and 150 cc of dry carbon disulphide were placed in a dry flask and cooled down to about zero and ferric chloride added in small amounts until five grams in all had been added. At first there was very little reaction but soon the reaction became quite violent even at the low temperature. Each addition of ferric chloride caused a considerable activity when introduced. Large amounts of halogen acid were evolved during the reaction.

The color of the solution turned from a light yellow, due to the bromal, to red, on the addition of a small amount of ferric chloride, then to brown, and later to green. The green is, probably due to the ferric chloride addition compound. The solution was allowed to stand for three days in the ice box after all action seemed to be complete and then warmed to room temperature and allowed to stand forty-eight hours more. The solution could not be heated as that decomposes the compound and complicates the reaction.

Then the carbon bisulphide solution was poured over finely divided ice and allowed to stand until the carbon disulphide had become clear and then the carbon disulphide was separated from the other and washed several times with acidified

19. Studies in Physical sciences and Mathematics of the U of M.

cold water to remove the traces of ferric chloride.

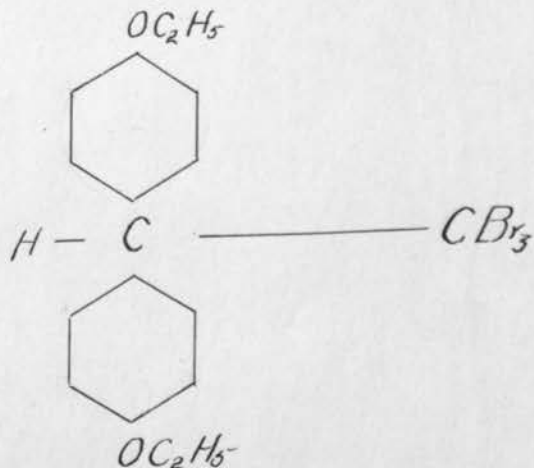
The carbon disulphide layer was separated and dried and then evaporated in a vacuum dessicator. The mass, when practically all of the carbon disulphide has been evaporated was a semi-solid, due to some of the unchanged phenetol. The mass was treated with ether and most of the oily substance was removed and on the addition of alcohol, the solid matter was precipitated, while the oil remained in solution. These impure crystals were filtered off and recrystallized from a small amount of ethyl acetate and alcohol and then recrystallized again from ether and alcohol. Pure white crystals were obtained in the form of hexagonal plates melting at 119° .

An analysis of the purified substance gave the following:

found

	I.	II.	III.	IV.
Carbon	42.54%	42.69%		
Hydrogen	3.70%	4.00%		
Bromine			47.36%	47.29%

This corresponds to the compound diphenetyltribromomethane.



This compound has been prepared from the action of phenetol and bromal in the presence of aluminium chloride by Frankforter and Kritchevsky²⁰ but because of the difference in melting point and color of the crystals the experiment was repeated.

Sixty-one grams ($\frac{1}{2}$ mole) of phenetol and seventy grams ($\frac{1}{4}$ mole)^{bromal} were dissolved in 250 cc of carbon disulphide and cooled down by a freezing mixture to below 0° C. Then twenty grams of chloride (aluminium) were added in about one half gram portions at intervals of about five minutes, the mixture being shaken after the addition of each portion. The solution turned a deep purple color and some purple crystals formed on the sides of the flask which when exposed to air were decomposed. When a small portion of the carbon disulphide solution was evaporated off in vacuo, the mass remained purple. When dried air was admitted, no change was noticeable in the color, but moist air changed them immediately. The above reaction mixture was allowed to stand twenty-four hours after no more evidence of reaction was noticeable even on the addition of another crystal of aluminium chloride. The mixture was allowed to take on room ~~pe~~ temperature to insure a complete reaction, but not heated so as to prevent side reactions and decomposition. After standing four hours, the mixture was poured over crushed ice and allowed to hydrolyze by means of the water that was dissolved in the carbon disulphide. In this case no tarry compounds were obtained as is the case if the water

20. J. A. C. S. 1914, 1526.

comes quickly in contact with the excess of aluminium chloride under which conditions a great amount of heat is evolved. After standing twelve hours the melting ice slowly furnishing the water for the hydrolysis the clear carbon disulphide solution of the compound remained at the bottom. This was separated by a separatory funnel and evaporated down to 100 cc. on the steam bath. When the solution cooled light yellow crystals were formed from the mother liquor. These were filtered out and washed with 95% alcohol and were white from the first crystallization. The mother liquor and alcohol were caught together, the alcohol causing precipitation of more of the compound which was added to the other and washed. The mother liquor and alcoholic washings were then caught together again. The crystals were dissolved in 200 cc. of ether and crystallized by evaporating the ether slowly. When it had evaporated down to 100 cc. alcohol was added to lessen the solubility of the crystals in the ether and also to cause the slight tarry color to remain in solution. These crystals were filtered off and washed with alcohol. The crystals were small hexagonal plates, colorless, and melted at 119° . Continued crystallization failed to raise the melting point. Crop. 64 grams. The washings and mother liquor were evaporated down, cooled and the crystals which were mixed with a tarry substance were filtered off and dissolved in a mixture of ethyl acetate and alcohol. The crystals slowly came out on allowing

the ethyl acetate to evaporate as almost colorless and large hexagonal plates, the tar remaining in solution. The crystals were filtered off and purified by crystallization from ether and alcohol. These separated out of the latter mixture as small hexagonal plates and had the same melting point. All of the filtrates from above were combined and concentrated, and again some solid was obtained, which was recrystallized from ethyl acetate and purified from ether. No more crystals were obtained from the tarry substance which amounted to five grams. The second and third crops combined weighed seven grams. The residual tarry substance was subjected to fractional distillation at 4 mm. pressure. 3.1 grams of unchanged phenetol came over and the residue decomposed giving off hydrogen bromide.

A determination of the molecular weight gave 490 and 500.

Analysis gave:

1. .3674 g. giving .5771 g of CO₂ and .1197 g of H₂O
2. .3826 g giving .5938 g of CO₂ and .1291 g of H₂O
3. .1127 g giving .1254 g of Ag Br.

Calculated for C₁₈H₁₉O₂Br₃:

		found		
		I.	II.	III.
C . -	42.60	42.81	42.50	
H. -	3.74	3.62	3.70	
Br. -	47.33			47.35

When a mixed melting-point was taken with the crystal obtained by Krichevesky and those obtained above, there was no lowering.

Crystals although in a much purer form were identical with those obtained by Krichevsky and Frankforter.

When these crystals are allowed to stand in a tightly stoppered tube exposed to the sunlight, a change in color is produced. they slowly take on a red color and no hydrogen bromide is evolved. These red crystals were set aside for future examination.

When 5.0 grms (1/100 mole) of diphenetyltribromethane were treated with an alcoholic solution of sodium alcoholate, with the idea of replacing some or all of the bromine with ethoxy groups and refluxed for six hours on a steam bath, a compound was formed in needlelike crystals when the solution was cooled. These were extremely soluble in alcohol and melted at 116° . They gave no test for halogen with a copper wire but when fused with sodium and the excess sodium decomposed by water and nitric acid, readily gave a test with silver nitrate.

Analysis gave the following:

1. .2122 g gave .3944 g of CO_2 and .0795 g of H_2O
2. .1173 g gave .1023 g of Ag Br

Calculated for $\text{C}_{18}\text{H}_{18}\text{O}_2\text{Br}_2$ as empirical formula - $\text{C}_9\text{H}_9\text{O}_2\text{Br}_2$

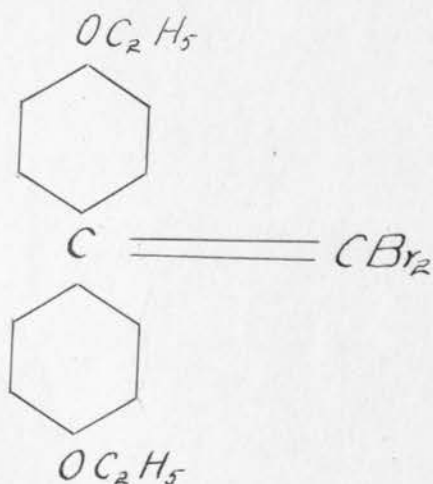
found

I.

II.

Carbon	50.7%	50.69%	
Hydrogen	4.2%	4.11%	
Bromine	37.5%		37.3%

As this would indicate that only hydrogen bromide was split out and no ethoxy groups were added, the compound would be diphenetyldibromethylene.



Five grams of diphenetyltribromethane were treated with sodium phenolate in absolute alcohol and refluxed for ten hours. Gradually everything went into solution and at the end of ten hours the reaction mixture was poured into acidified water to decompose the unchanged sodium phenolate and also to dissolve the sodium bromide formed in the reaction. The organic substance that was precipitated was washed several times with hot water to remove the last traces of inorganic material. It formed needlelike crystals which melted at 116° . These gave a slight test for halogen. Then because of their melting point being the same as that of diphenetyldibromethylene, I ran an analysis which gave me the following:

1. 0.2175 gave 0.4043 g of CO_2 and .0822 g of H_2O
2. 0.2277 gave 0.2006 g of Ag Br

Calculated for $(C_6H_4OC_2H_5)_2 C - C Br_2$

	found	
	I.	II.
Bromine	37.5%	37.49%
Carbon	50.7%	50.68%
Hydrogen	4.2%	4.2%

From this I concluded that the sodium phenolate had the same action of splitting out hydrogenbromide as alcoholic potash.

When five grams of diphenetyltribromethane were refluxed with potassium cyanide in absolute alcohol, a crystalline substance melting at 116° was obtained again. This was found to be the diphenetyldibromethylene. A determination of bromine indicated that the same compound was obtained.

An analysis gave the following result:

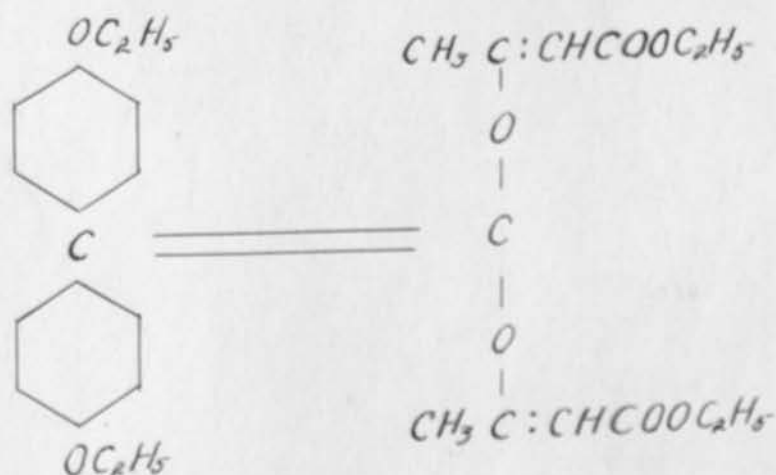
1. 0.1127 g of substance gave .0993 g of Ag Br.

That calculated for diphenetyldibromethylene gives 37.5% bromine and this gave 37.49% bromine.

Since the alcohol must have been the cause of the reaction going this way, ten grams of dry sodium phenolate, five grams of the diphenetyltribromethane, and twenty cubic centimeters of dry ether were placed in a flask and the mixture refluxed for forty-eight hours, and treated with water. No apparent reaction had taken place as five grams of the original substance were obtained after decomposing the reaction mixture. This would

tend to show the stability of the bromine in the compound or that the temperature was not high enough to give enough to give a reaction.

Diphenetyl-diaceto-acetyl-ethylene



Two grams of sodium were dissolved in twenty five grams of acetoacetic ether to prepare the sodium salt of aceto-acetic ether. To this mixture was added 4.2 grams of diphenetyldibromethylene and the reaction mixture refluxed for forty-eight hours. After that time the reaction mixture was decomposed by pouring the mixture into water acidified with hydrochloric acid. Crystals were formed which were washed with warm water and crystallized from alcohol in long needlelike crystals melting at 168° . A second crystallization gave colorless crystals that melted at 169° .

The 'C' compound may be also considered in equilibrium with the above compound and still give the same results given below.

An analysis gave the following:

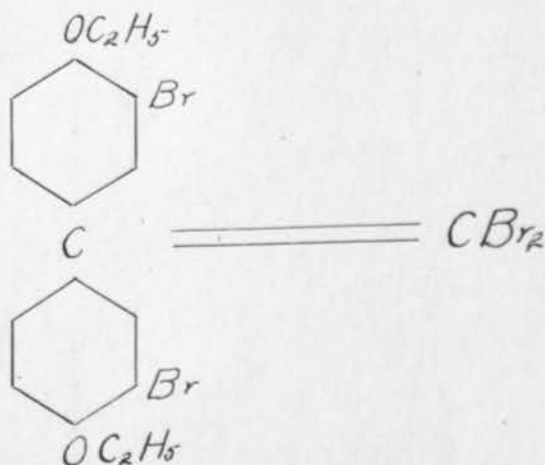
- 0.1094 g of substance gave .2757 g of CO_2 and .0626 g of H_2O
- 0.1950 g of substance gave .4912 g of CO_2 and .1206 g of H_2O

Calculated for $\text{C}_{30}\text{H}_{36}\text{O}_8$

found

		I.	II.
Carbon	68.70%	68.74%	68.69%
Hydrogen	6.87%	6.42%	6.90%

Di-ortho-brom-phenetyl-dibrom-ethylene



Four grams of diphenetyldibromethylene were dissolved in ten cc. of glacial acetic acid and bromine added. Fumes of hydrogenbromide were given off. When the action had stopped the excess bromine was removed by warming the mixture and drawing air through it. When the solution became clear, a small amount of alcohol was added to the acetic acid solution and then the mixture was allowed to crystalize. White crystalline plates

were formed that melted at 106° . These were recrystallized from alcohol and ether and melted at 120° .

An analysis for bromine gave the following:

0.1216 grams of substance gave 0.1560 grams of Ag Br

Calculated for $C_{18}H_{16}O_2Br_4$

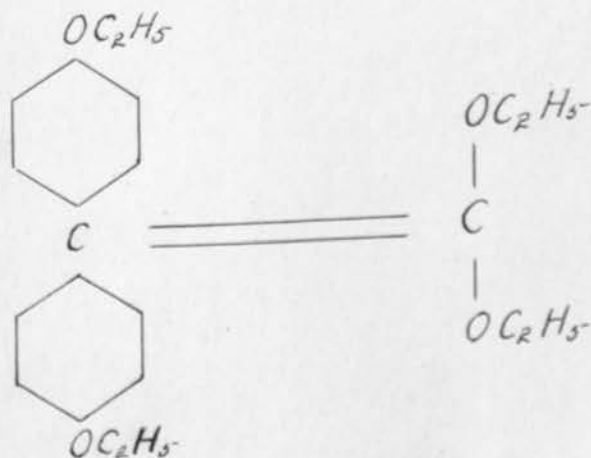
found

I.

Bromine 54.79%

54.60%

Diphenetyl-diethoxy-ethylene



Five grams of diphenetyltribromethane were placed in a flask containing twenty grams of sodium alcoholate and twenty cc. of thiophene free benzene that had been dried over sodium. The sodium alcoholate was not apparently soluble in the benzene, so that the reaction mixture had to be refluxed for a longer time. After the mixture had been refluxed for forty-eight hours, the reaction mixture was poured slowly into ice water acidified with hydrochloric acid. The benzene solution was washed several times with water and separated in a separatory funnel. The

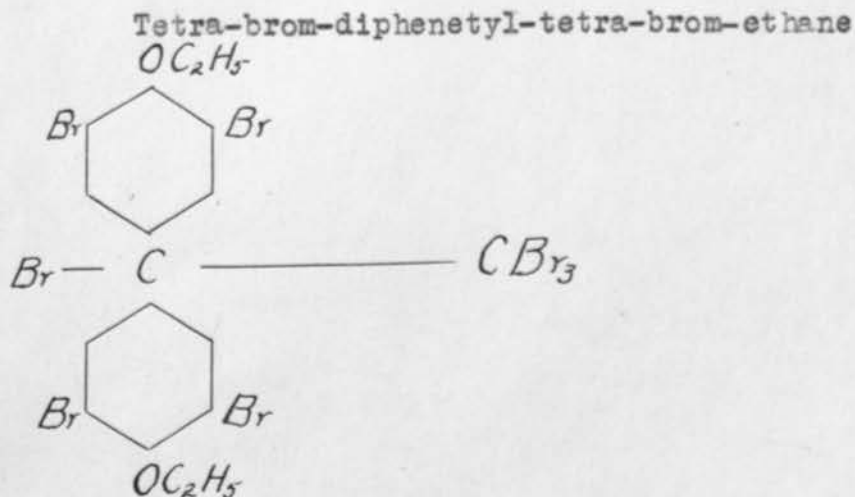
benzene solution was dried and finally evaporated down to ten cc. when crystals were formed which were very impure. These, as well as the impurities, were very soluble in all the common solvents. Ligroin was found to purify the crystals. They were crystallized three times from ligroin and then from 80% alcohol. These were formed in short needlelike crystals having a melting point of 96° to 97°. This compound had a very distinct aromatic odor, that has not been observed in working with any related compounds.

Analysis of the purified crystals were as follows:

1. 0.2085 g gave .5672 g of CO₂ and .1474 g of H₂O
2. 0.3148 g gave .8925 g of CO₂ and .2494 g of H₂O

Calculated for C₂₂H₂₈O₄

		found	
		I.	II.
Carbon	74.15%	74.14%	7.8%
Hydrogen	7.86%	74.1%	7.9%



Two and one half grams of diphenetyl-tribromethane were dissolved in glacial acetic acid and bromine added in excess. This solution was allowed to stand for eight hours and then the excess bromine was removed by drawing air through the solution. The acetic acid was allowed to evaporate spontaneously and a colorless oily substance was precipitated which crystalized when dissolved in ether and the ether evaporated slowly. The crystals were colorless, melting at 68° .

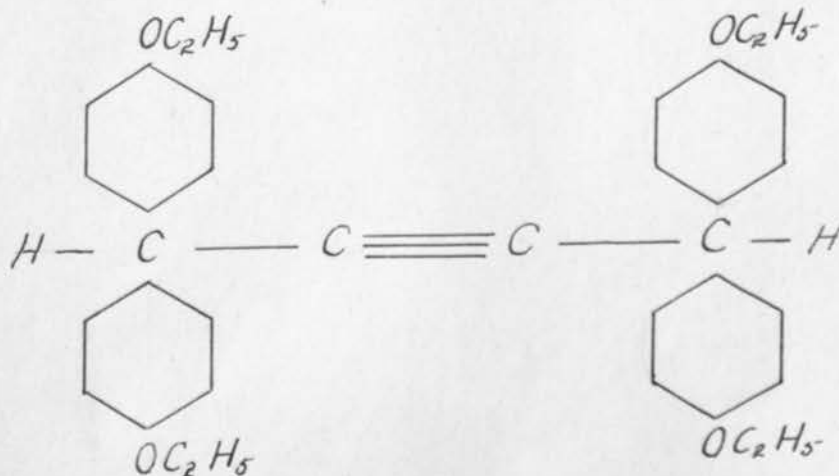
Analysis for bromine gave the following:

0.1483 g gave 0.2472 g of Ag Br

Calculated for $C_{18}H_{14}O_2Br_8$

	found
Bromine 79.95%	79.9%

Di-diphenetyl-methyl-acetylene



Ten grams of diphenetyltribromethane and twenty grams of sodium powder were placed in a flask containing forty grams of dry thiophene free benzene. The mixture was refluxed on a

steam bath for seventy-two hours and the benzene solution poured off, and evaporated down to twenty cc. On cooling, a white substance almost insoluble in cold benzene was precipitated. This compound was very slightly soluble even in hot alcohol but dissolved in a boiling mixture of one part of absolute alcohol to two parts of benzene. From this mixture beautiful colorless plates were formed melting at 202° . A second crystallization from the same kind of mixture changed the melting point to 203° , where it melted very sharply. Crop, 3.8 grams.

A molecular weight determination by the freezing point method gave the following results.

508 - 530 - 525 - The calculated is 522.

An analysis of the high melting point substance gave the following:

0.1280 g of substance gave .3791 g of CO_2 and .0820 g of H_2O

0.1240 g of substance gave .3679 g of CO_2 and .0798 g of H_2O

Calculated for $\text{C}_{35}\text{H}_{38}\text{O}_4$

		found	
		I.	II.
Carbon	80.89	80.8%	80.9%
Hydrogen	7.11	7.1%	7.15%

When the mother liquor from the above was evaporated down and cooled, again a substance containing no bromine and soluble in the ordinary solvents crystallized out in needlelike crystals melting at 158° to 159° . Crop, one half gram. This

compound was set aside to be examined later.

Later diphenetyl-dibrom-ethylene was treated with sodium powder in pure dry benzene for eight hours. A needlelike crystalline compound was obtained when the benzene was filtered off and evaporated. These crystals were dissolved and recrystallized from a small amount of hot alcohol. These melted at 158° to 159° , as those in the above reaction did. These were set aside to be taken up later.

Summary.

I. It will be seen that ferric chloride has much the same action on bromal and phenetol as aluminium chloride. The only exception is that the yields are lower.

II. The properties and derivatives of diphenetyl-tri-brom-ethane are as follows:

a. An alcoholic alkaline solution first takes out hydrogen bromide, leaving the unsaturated compound, diphenetyl dibromethane.

b. When brominated, five of the hydrogens are displaced giving tetra-brom-diphenetyl-tetra-brom-ethane.

c. When treated for a long time with sodium salts of ethyl alcohol and acetoacetic ester, the unsaturated compound diphenetyl-dibrom-ethane is first produced, and then the group is substituted for the two remaining bromines giving diphenetyl-diethoxy-ethylene and diphenetyl-diacetoacetyl-ethylene respectively.

d. The action of a Wurtz^{synthesis} on diphenetyl-tribrom-ethane gives an ethylenic substitution compound, di-diphenetyl-methyl-acetylene.

III. The derivatives of di-phenetyl-dibrom-ethylene were as follows:

a. Treating with sodium alcoholate and sodium acetoacetyl ester gave the same compounds as the saturated compound.

b. Bromine displaced two hydrogens on the ring, but did not add to the double bond, forming di-ortho-brom-phenetyl-dibrom-ethylene.

c. Treating with metallic sodium gave compound which has not been identified.

* * * * *

This work was done under the direction of Dr. G.B. Frankforter of the University of Minnesota.