THE DECOMPOSITION OF DI-o-TOLYLIODONIUM IODIDE

Thesis by
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Contents of this Thesis

Two possible mechanisms are postulated for the thermal decomposition at 150 of di-ortho-tolyliodonium iodide. The most likely involves (a) the decomposition of the o-Tolyliodonium ion into o-Iodotoluene and positive o-Tolyl ion and (b) the uniting of this ion with the negative iodide ion to form o-Iodotoluene. The reaction products of this decomposition were converted into Toluic acid by the Grignard reaction and shown to be ortho-Toluic acid. The most important aspect of this decomposition is the existence of a positive o-Tolyl ion.

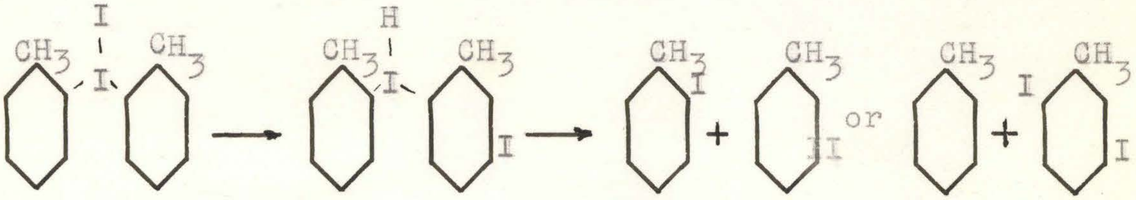
o-Iodotoluene was prepared and converted into o-Iodosotoluene. The oxidation of iodosotoluene to iodoxytoluene by means of hypochlorite was studied. A new method of preparing iodonium compounds was applied in the preparation of di-o-tolyliodonium iodide. The conversion of iodotoluene to toluic acid using small quantities was studied.

THE DECOMPOSITION OF DI-o-TOLYLIODONIUM IODIDE

INTRODUCTION

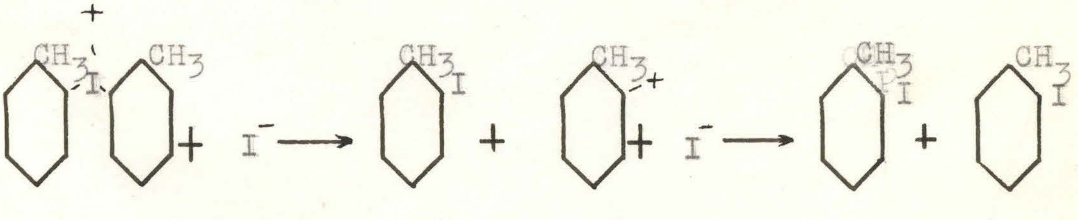
When di-o-tolyliodonium iodide undergoes thermal decomposition into tolyl iodide the product might be either a mixture of the ortho and meta isomers or else the pure ortho isomer alone, depending upon whether the reaction took one of the two following courses; (a) rearrangement, followed by decomposition, or (b) decomposition into ions, followed by combination of the ions. The two possibilities are shown below:

(a) REARRANGEMENT FIRST



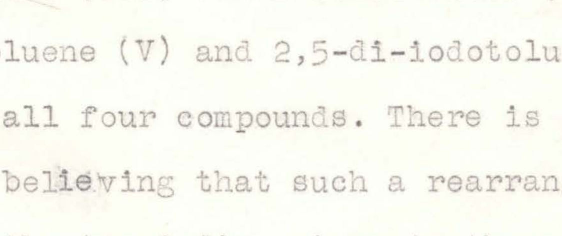
I II III IV V VI

(b) DECOMPOSITION FIRST



VII VIII IX X

When an electronegative radical is attached to a nitrogen or oxygen atom directly linked to a carbon atom of the benzene ring, molecular rearrangement is usually possible by the migration of such a radical to an ortho or para position in the benzene ring. Since in general the oxygen compounds undergo rearrangement more readily than the nitrogen derivatives it seems reasonable to assume that the more electronegative the atom to which the migrating radical is attached, the more readily rearrangement will take place. On such a basis alone, one might expect a migration of the iodide iodine atom to a position in one of the benzene rings ortho or para to the iodonium iodine atom. The compound represented by formula II above would result if para migration takes place. Decomposition of this intermediate would lead to the production of a mixture of O-iodotoluene (III) and m-iodotoluene (IV) or to a mixture of toluene (V) and 2,5-di-iodotoluene (VI) or to a mixture of all four compounds. There is some <u>a priori</u> evidence for believing that such a rearrangement is not likely since the two iodine atoms in the molecule of ditolyliodonium iodide are not joined to each other by a covalent bond. The compound is a salt and has the following electronic structure:



On this basis the migration of iodine to the para position would appear to be as unlikely as the migration of chlorine in phenylammonium chloride.

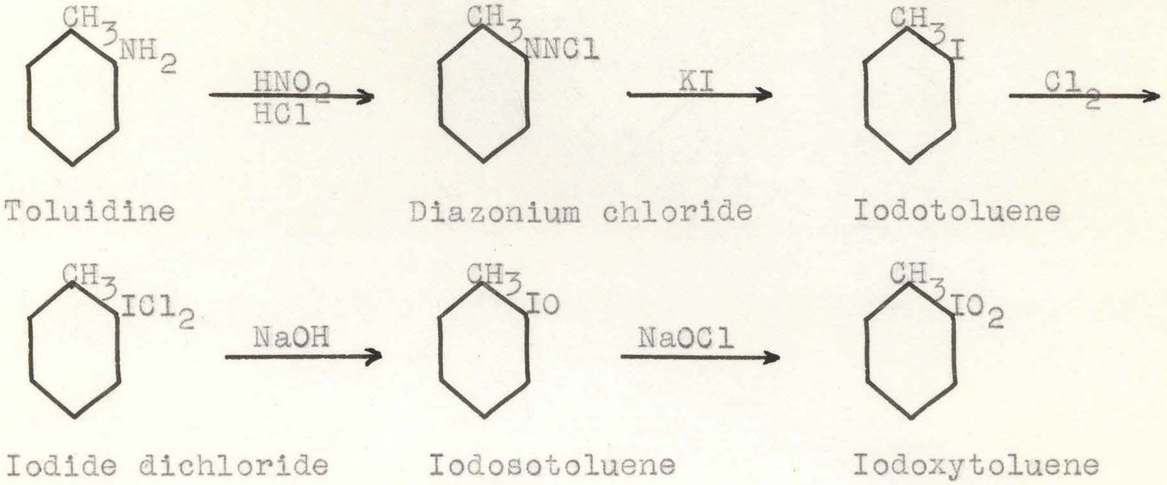
If di-o-tolyliodonium iodide suffers decomposition in the second series of changes above, then the positive di-o-tolyliodonium ion(VII) must decompose into o-iodotoluene (VIII) and positive o-tolyl ion (IX). Provided the latter undergoes no subsequent change it would then unite wi with the negative iodide ion to produce o-iodotoluene (X). The product in this case would be pure o-iodotoluene. A determination of the nature of the reaction products would make possible a decision in favor of one of the two possible mechanisms[1].

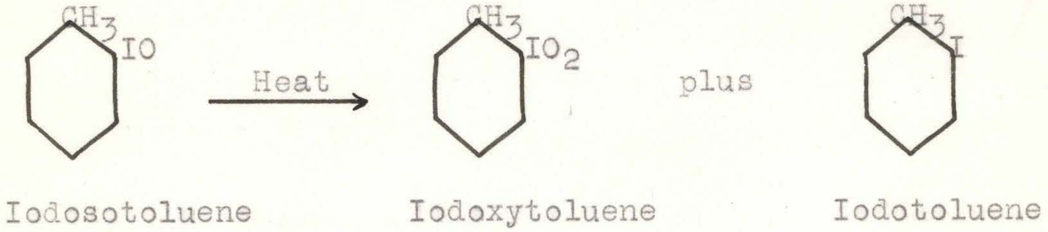
Many years ago Heilbronner[2], investigating this reaction, concluded that di-o-tolyliodonium iodide was changed into *ortho* iodotoluene, which was identified by conversion into nitro-iodotoluene. Since no statement appears in regard to which nitro compound was formed nor the amount obtained upon nitration, it is quite possible that other reaction products might have been present in the reaction mixture and yet have been overlooked by him.

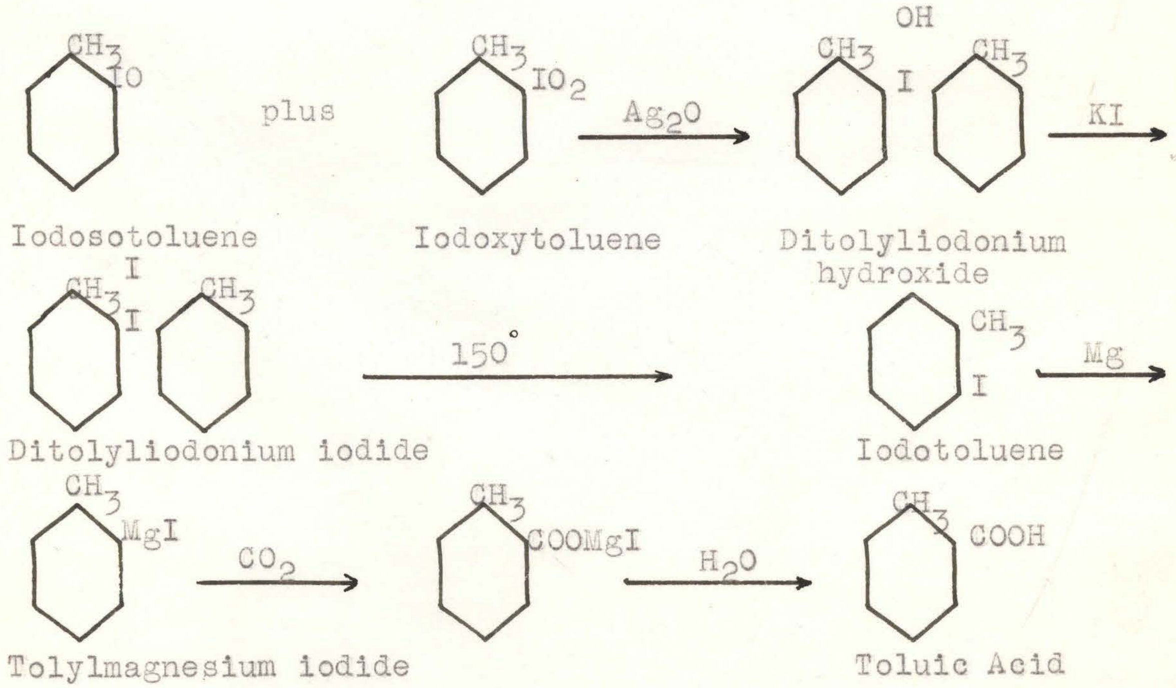
In the present research the iodotoluene produced in the decomposition was converted into the corresponding toluic acid through the reaction of carbon dioxide upon the tolyl magnesium iodide, The resulting acid was definitely shown to be pure *ortho* acid. This result confirms the conclusions of Heilbronner, and of Wilmot[3] who did some work on this problem, and indicates that the decomposition proceeds according to the second mechanism given above.

The most important aspect of this decomposition is the existence of a positive ortho-tolyl ion.

OUTLINE OF EXPERIMENTAL PROCEDURE







EXPERIMENTAL

Part I The preparation of Di-o-tolyliodonium iodide

A. The preparation of pure o-iodotoluene.

The starting material for this step in the synthesis was o-toluidine, $CH_3C_6H_4NH_2$. This material was purified of other isomers according to the method of Beilstein[4]. The procedure was as follows: 400 grams of o-toluidine was dissolved in 800 ml. of 6N nitric acid. The solution was filtered boiling hot and allowed to cool. The fine crystals which formed were filtered off and redissolved in the minimum quantity of boiling water, norite decolorizing carbon added and the solution filtered hot. After cooling the crystals, which were large purplish plates, were filtered off and the mother liquor used to dissolve another batch of o-toluidine nitrate prepared as above. The crystallization was continued until each batch had been recrystallized three times, using the mother liquor from the first batch to crystallize the second batch in each case. The crystals were sucked dry on a filter and weighed. Yield was 982 grams (77.3% of original toluidine). The toluidine was freed from the nitric acid by adding 250 grams sodium hydroxide (slight excess), together with enough water to dissolve the sodium nitrate formed, and the mixture submitted to steam distillation. The toluidine was then separated from the aqueous phase in the distillate. The product thus obtained was colorless, but slowly became red over a long period of time due perhaps to oxidation by oxygen of the air, action of light, etc.

o-Iodotoluene was prepared from this toluidine by the diazo reaction, using 10% sodium nitrite solution (to which had been added a small quantity of sodium meta bisulphite to reduce any nitrate present). The end point of the reaction was determined with starch-iodide paper. Upon adding potassium iodide solution to the diazonium solution the iodotoluene separated as a dark oil.

The o-iodotoluene from the first three runs was combined for the purposes of purification. It was rapidly distilled at atmospheric pressure. This treatment left an oily black tar in the distilling flask.(probably cresol). The orange colored distillate was washed in a separatory funnel as follows: 1. NaOH 2. NaOH 3. H_2O 4. HCl 5. HCl 6. H_2O 7. Very dilute NaOH 8. H_2O 9. H_2O 10. H_2O. This gave a clear oily liquid which was dried with anhydrous sodium carbonate and vacumn distilled at 24 mm. The product was a colorless liquid which was kept in a glass stoppered bottle filled with nitrogen, as otherwise a pink color develops on standing,due to oxidation.

B. The preparation of meta and para iodotoluenes.

As it was later found necessary to prepare meta and para iodotoluenes, their preparation will be included here for the purposes of comparison.

m-Iodotoluene was prepared as above from m-toluidine which was obtained from meta nitrotoluene. The m-nitrotoluene was purif uene was purified by three crystallizations (m.p. 16°). The m-nitrotoluene was converted into m-toluidine by the action of tin and hydrochloric acid, followed by neutralization of the acid and steam distillation.

m-Nitrotoluene	75.0 grams
m-Toluidine	53.5 grams (91.5%)

The p-iodotoluene was obtained from Eastman's practical p-toluidine.

Table I contains the results of these preparations. Physical constants determined for the compounds are in Table II.

TABLE I * PREPARATION OF IODOTOLUENE

Toluidine		Iodotoluene		
run	grams	grams crude	grams redistilled	%
1. ortho	50	85	(60)	-
2. ortho	125	218	(154)	-
3. ortho	125	209	(147)	-
1, 2, 3.	300	512	361	59.1
4. ortho	83	-	138	81.5
5. ortho	60	-	100.5	82.0
6. meta	35	-	54.5	76.5
7. para	50	-	76.0	74.6

TABLE II * PHYSICAL CONSTANTS IODOTOLUENES

Iodotoluene	ortho	meta	para
B.P. 745 mm	205.5°	210.0°	-
24 mm	95.5	-	-
Sp. Gr. 20/20	1.7090	1.6981	-
n_D	1.6030	1.6012	-
M.P.	-	-	34.5-35.0°

C. The preparation of iodosotoluene $CH_3C_6H_4IO$

o-Iodosotoluene was prepared from the purified o-iodotoluene by a slight modification of the method of Willegerodt[5]. A solution of iodotoluene in anhydrous chloroform (dryed by means of calcium chloride and distilled after separating off the solid) was made up in the ratio of 2ml. chloroform to one gram iodotoluene. If a more dilute solution is used an unnecessary amount of chloroform is wasted as will be seen, while if a more concentrated solution is used it becomes difficult to stir with a consequent failure to secure complete reaction. Chlorine, dryed by passing through two concentrated sulphuric acid wash bottles and then through a tube containing phosphoric anhydride, was led onto the surface of the solution in a closed flask and vigorous stirring applied to cause solution of the gas. (If the gas entry tube dips below the surface of the solution it very quickly plugs up). The flask is cooled during the passage of the gas.

When the solution is saturated with chlorine (in about 2½ hours), it is placed under vacumn and practically all of the chloroform evaporated at room temperature. The remaining chloroform (about 10% of the original) is sucked off from a filter and the dry yellow crystals of iodotoluene dichloride placed in a mortar and rubbed with a solution of sodium hydroxide (1 gram NaOH to 8 ml. H_2O) in slight excess of the amount calculated according to the following equation

$$CH_3C_6H_4ICl_2 + 2\ NaOH \longrightarrow CH_3C_6H_4IO + 2\ NaCl + H_2O$$

The iodosotoluene is filtered off, washed with water and chloroform and dryed. The purity was determined by iodimetry according to a method developed by Wilmot[3]. The distinguishing feature of this method is the addition of a small quantity of chloroform at the beginning of the titration reaction, otherwise the solid iodine compound reacts but slowly possibly because its surface becomes coated with reaction products which are insoluble in water but dissolve in the chloroform.

By saturating the alkaline filtrate from the preparation of iododsotoluene with sulfur dioxide and/or adding a small amount of potassium iodide a small quantity (3-5% of original iodosotoluene) may be recovered.of di-ortho-tolyliodonium iodide.

TABLE III * PREPARATION OF IODOSOTOLUENES

Iodotoluene	grams	Iodosotoluene grams	%
1. ortho	109	83	71.0
2. ortho	50	41	76.5
3. ortho	70	51.7	64.0
4. ortho	90	70	73.0
5. meta	20	16.3	76.0
6. para	25	17.0	64.0

note: The yield to a very large extent depended upon the amount of chloroform rejected in the separation of iodotoluene dichloride, as it is quite soluble in this solvent.

TABLE IV * ANALYSIS OF IODOSOTOLUENES

	Sample grams	0.1N.Thio. ml.	Found grams	Strength %	Drying Procedure
1. ortho	0.156	12.49	0.143	92.8	36 hr. in air
2a ortho	0.345	26.80	0.313	91.0	2 days in air
b	0.0995	7.90	0.0924	92.8	9 days in air
c	0.231	19.65	0.230	99.6	2b in vacumn 12 hr.
3a ortho	0.068	5.42	0.063	93.2	4 days in air
b	0.0847	7.43	0.0870	102.5	3b in vacumn 12 hr.
4. ortho	0.379	28.81	0.337	89.0	1 day in air
5. meta	0.380	29.05	0.340	89.4	1 day in air
6. para	0.207	15.46	0.181	87.4	2 days in air

This data is interpreted to mean that when iodosotoluene is dryed in air the compound obtained is $CH_3C_6H_4(OH)_2$, which compound corresponds to 92.9% oxidizing strength when calculated as $CH_3C_6H_4IO$. On vacumn dessication the bonded water is lost and the iodosotoluene obtained. Since iodosotoluene slowly decomposes into iodotoluene and iodoxytoluene, removal of the iodotoluene will result in a compound of apparent oxidizing strength greater than 100%, since the iodoxytoluene has twice the oxidizing strength on a molal basis of iodosotoluene. Thus the value of 102.5% above indicates a purity of about 97.6% for the iodosotoluene.

D. The Preparation of Iodoxytoluene.

An attempt was made to use a modification of Willegerodt's method[6], which had been worked out by Wilmot. It consisted in mixing iodosotoluene and pure calcium hypochlorite with just enough water to make a thin paste and passing carbon dioxide slowly into the mixture with stirring. If the gas was passed too rapidly chlorine was formed in the reaction mixture. The reaction usually required two to three days for completion. The reaction mixture was washed with 1N nitric acid, with water and with chloroform. The purity of the iodoxytoluene was determined as before by iodimetry, calculating the oxidizing strength as $CH_3C_6H_4IO_2$. Yields were calculated according to the following reactions:

$$\begin{array}{l}
Ca(OCl)_2 + H_2CO_3 \longrightarrow CaCO_3 + 2\,HOCl \\
2\,CH_3C_6H_4IO + 2\,HOCl \longrightarrow 2\,CH_3C_6H_4IO_2 + 2\,HCl \\
2\,HCl + CaCO_3 \longrightarrow H_2CO_3 + CaCl_2 \\
\hline
2\,CH_3C_6H_4IO + Ca(OCl)_2 \longrightarrow 2\,CH_3C_6H_4IO_2 + CaCl_2
\end{array}$$

The results of several trial runs are presented in table V

TABLE V * OXIDATION OF IODOSOTOLUENE BY HYPOCHLORITE

	Weight C_7H_7IO gr.	Hypochlorite mols	CO_2	Stirring time days	Yield gr.	%	Oxidizing strength %
1.	10	4 $Ca(OCl)_2$	*	2	2.3	22	83
2.	10	4 $Ca(OCl)_2$ in 4 pts	*	2½	2.1	20	175
3.	10	1 NaOCl, 1 $Ca(OCl)_2$	*	2	3.7	35	148
4.	10	1.1 NaOCl	*	3½	1.9	18	78
5.	10	4 $Ca(OCl)_2$ in 4 pts	*	½	3.5	33	95
6.	10	1.5 NaOCl	no	4	4.2	40	99
7.	10	1.5 NaOCl	no	2	3.7	36	97
8.	C_7H_7I	1.3 NaOCl		15	extremely slow		

Recalculation of the titration data on the assumption that the product is $CH_3C_6H_4IO_3$ or $CH_3C_6H_4IO_4$ gives the values shown in Table VI. From these calculations it seems as if #2 is $CH_3C_6H_4IO_4$ and #3 is largely $CH_3C_6H_4IO_3$ or a mixture of $CH_3C_6H_4IO_3$ and $CH_3C_6H_4IO_4$. At present no further data is available regarding the composition and structure of these compounds.

TABLE VI * CALCULATION OF OXIDIZING POWER

	$CH_3C_6H_4IO_2$	$CH_3C_6H_4IO_3$	$CH_3C_6H_4IO_4$
#2	175	124	99
#3	148	105	83

As may be seen from Table V the yields are low and the oxidizing strength of the product depends largely upon the experimental conditions. For this reason it was decided to use the standard procedure for preparing iodoxy compounds, which consists in heating iodosotoluene with water. A further advantage of this method lies in the fact that iodotoluene steam distills out of the mixture and may be recovered. It was found possible to recrystallize the iodoxytoluene from hot water. In one such experiment the following data were obtained:

Iodosotoluene	Iodoxytoluene		Iodotoluene	
grams	grams	%	grams	%
50	19.5	38	16.8	36

Titration data- $CH_3C_6H_4IO_2$

sample gr.	0.1N Thio. ml.	found gr.	strength %	drying procedure
0.219	17.09	0.214	97.5	2 days in air

E. The Preparation of Di-o-tolyliodonium iodide.

Two attempts were made to prepare this compound by the method of Meyer and Hartmann[7] who reported yields of 93% for phenyliodonium iodide. Equimolal quantities of iodosotoluene and iodoxytoluene were treated with water and an excess of freshly precipitated silver oxide by agitating in a glass stoppered bottle for two days. After filtering off silver oxide and any unreacted material, the filtrate was reduced with sulphur dioxide, but only a negligible precipitate was obtained. In a similar experiment using a smaller quantity of water a precipitate of ditolyliodonium iodide was obtained which corresponded to a yield of 18% of theoretical.

It was decided to modify the procedure somewhat and the following was tried. 9.3 grams (0.038 mol) of $C_7H_7IO_2$, 9.0 grams (0.038 mol) of C_7H_7IO, 10 grams (0.043 mol) of silver oxide, 10 ml. of chloroform and a small quantity of water were ground together in a mortar. At intervals the water was poured off into a flask and more water added to the mixture in the mortar. Finally the pasty mass remaining was left to react overnight. The collected aqueous portions were filtered and reduced with sulphur dioxide which caused the immediate formation of a white precipitate. A small amount of potassium iodide was added to ensure the complete precipitation of the compound. The precipitate was filtered and washed with water and alcohol. Yield was 7.0 grams (44.0%). Chloroform was added because it was thought that it would aid the reaction by dissolving water-insoluble intermediate products.

The above procedure was repeated with the exception that only 5% of the molal quantity of silver oxide was used. The yield in this case was practically the same as before (43.5%). This would seem to indicate that the silver oxide acts merely as a catalyst and is not required in molal quantities as is usually reported. The fact that the yield is but 44% as compared to 93% for the phenyl compound may possibly be attributed to the steric influence of the methyl group in the ortho position. None of the investigators who prepared the o-tolyl compound reported yields.

F. The Preparation of Toluic Acid from Iodotoluene.

Before proceding with the decomposition of the di-o-tolyliodonium iodide it was thought advisable to determine the conditions necessary for an optimum identification of the products by conversion of the iodotoluene to Toluic acid by the Grignard reaction. Accordingly pure iodotoluene was dissolved in anhydrous ether and slowly run onto magnesium in anhydrous ether with stirring. After sufficient time for complete reaction,carbon dioxide, dried by passing through concentrated sulphuric acid and then over phosphoric anhydride,was passed in with external cooling of the reaction flask. When no more carbon dioxide was absorbed, ice and a 100% excess of 6N sulphuric acid was added. The ether phase was separated off and the aqueous phase extracted with three successive portions of ether. The combined ethereal phases were extracted with four sucessive portions of 2N sodium carbonate solution in the ratio of 4/2/2/1. The combined sodium carbonate solution extracts were heated to remove dissolved ether, cooled and acidified with C.P. sulphuric acid. The precipitated Toluic acid was dried and weighed. No loss is introduced by solubility of the toluic acid in water as the solubility at room temperature is less than 0.04 gram per 100ml. The results of several such runs are shown in Table VII. The extracted

TABLE VII * THE PREPARATION OF TOLUIC ACID

Iodotoluene		Mg	Ether conc.	Toluic acid		Rate of
	gr.	mols	ml/gr.	gr.	%	stirring
1. ortho	10.4	1.0	7.7	3.2	49	slow
2. ortho	8.2	1.0	12.2	2.6	51	fast
3. ortho	8.0	1.0	27.5	2.4	47	moderate
4. ortho	8.5	1.0	8.2	2.2	42	"
5. iodobenzene		1.0	6.4	-	52	"
6. meta	8.2	1.1	9.8	2.3	44	fast
7. meta	6.1	1.3	16.1	1.8	47	moderate
8. meta	6.7	1.3	12.0	1.6	38	"
9. para	6.1	1.3	16.0	2.1	55	"
10. ortho	11.3	1.2	6.3	5.4	77	"

(note: iodotoluene added very slowly in #4)

ether solution was evaporated and the thick semi-solid oil obtained is thought to be o-o'-ditolyl (m.p. 17.8°).

It was first thought that the low yield (should be of order of 80 % for iodobenzene) was to be ascribed to coupling reactions of the Grignard reagent to form ditolyl. Changes in the experimental procedure designed to reduce this coupling reaction gave no better yields. It was next thought that the low yield was due to the steric hindrance of the methyl group but experiments with iodobenzene, meta iodotoluene, and para iodotoluene showed the same poor yield. It was finally concluded that the low yields were caused by the presence of minute quantities of water, since it reacts with the Grignard reagent. A calculation showed that the presence of 0.15 gram of water would lower the yield by about 50% on the basis of the quantities used.

Methyl iodide was placed in the flask with the magnesium and ether and allowed to react for an hour. This reacts in a similar manner with water as does iodotoluene but much more rapidly. The toluic acid preparation was then carried out as before. The result of this run is shown in #10 above and the yield was markedly improved and compares favorably with the literature value for iodobenzene using much larger quantities. The methyl iodide added was just that amount to react with the supposed water present. (CH_3I = 0.90 ml). This water is probably present adsorbed on the walls of the apparatus, minute amounts in the ether, etc. Any excess of methyl iodide will form acetic acid, and there is also the possibility of the formation of xylene with iodotoluene.

These experiments also show that the three isomeric iodotoluenes react with equal facility to form toluic acid under these conditions. This observation lends strength to the conclusions drawn later regarding the identity of the decomposition products of di-o-tolyliodonium iodide.

Part II The Decomposition of Di-o-tolyliodonium iodide.

Preliminary experiments showed that the di-o-tolyliodonium iodide did not decompose until raised to 150°. In carrying out the decomposition 16.38 grams were placed in a 100 ml flask provided with a reflux condenser and immersed in a glycerine bath at 155°. After about two minutes decomposition set in and was complete inside of five seconds. There was a loss of weight of 0.11 grams on decomposition and this may be attributed to the portion adhering to the lower end of the condenser. The amount of toluene produced in this decomposition could not have been over 0.11 gram, otherwise it would have distilled out of the reaction product and collected in the condenser, from which no liquid ran back. There was a small amount of iodine vapor in the flask. The decomposition product was transfered to a glass weighing pipet. No attempt was made to purify the product.

Part III The Identification of the Decomposition products.

The index of refraction was determined.

n_D 1.607

The free iodine was determined by titrating with sodium thiosulphate solution.

Sample gr.	0.024 Thio. ml.	Iodine gr.	%
1.183	1.55	0.0045	0.38

14.38 gr.(0.066 mol) of the decomposition product in 15 ml. of anhydrous ether was run during the course of three hours onto 1.8 gr.(0.074 mol) of magnesium in 70 ml. of ether (which had reacted for one hour with 0.90 ml. methyl iodide) contained in a 200ml. 3-neck flask provided with a mechanical stirrer, reflux condenser, and separatory funnel. The stirring was continued another three hours. Dry carbon dioxide was passed in for three hours with stirring. The acid was extracted as described above,, dryed in a vacumn dessicator, and weighed. Yield was 5.75 gr. (0.042 mol) or 64%.

The crude acid melted at 102.4-103.0°. A mixture of this with ortho-toluic acid (obtained in the above trial runs and recrystallized from hot water. M.P. 103.5-103.7°) melted at 102.5-103.0 , while a mixture made with meta-toluic acid (M.P. 110.6-111.2°) melted at 65-91°, and a mixture with para-toluic acid (M.P. 178.5-178.8°) melted at 86-146°. This indicates that the product was <u>pure</u> ortho-toluic acid.

When the ether solution from which the toluic acid had been extracted was evaporated 1.55 grams of a pasty oil was obtained. If this be calculated as ditolyl it represents 3.7 gram or 25% of the decomposition product. This brings the decomposition products accounted for to 89%. Circumstantial evidence may be presented to show that this oil was formed during the grignard reaction rather than during the decomposition of the di-o-tolyliodonium iodide itself. Briefly this evidence is:

1. If ditolyl were formed in the decomposition

there would be an equivalent amount of iodine set free. The amount of free iodine actually shown to be present would account for only 0.04 gr. of the 1.55 gr. found.

2. This oil resembled in physical appearance those byproducts obtained in a similar fashion from <u>pure</u> ortho-iodotoluene.

3. The refractive index of a 10% solution of the oil in o-iodotoluene was: n_D 1.592

(Decomposition product n_D 1.607

o-Iodotoluene n_D 1.6030)

Thus the addition of the oil changes the refractive index in the opposite direction from which it should change to coincide with the decomposition product.

The isolation of ortho-toluic acid unmixed with other isomers shows that ortho-iodotoluene is the sole product of the decomposition of di-o-tolyliodonium iodide.

I wish to express my deepest thanks to Prof. H.J.Lucas, who suggested this problem, for his continued interest and advice.

SUMMARY

When di-o-tolyliodonium iodide undergoes thermal decomposition at 150° it is converted into o-iodotoluene. This was established by converting into an acid which was shown to be o-toluic acid.

The most likely mechanism of the reaction involves
(a) the decomposition of the tolyliodonium ion into o-iodotoluene and positive o-tolyl ion and
(b) the uniting of this ion with the negative iodide ion to form o-iodotoluene.

The oxidation of o-iodosotoluene by aqueous hypochlorite was investigated.

A new method of preparing iodonium compounds is described.

The optimum conditions for the conversion of iodotoluene to toluic acid in good yield when working with small quantities was investigated.

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