

between 132.2 and 132.4° and was shown to be chlorobenzene by converting it into *p*-bromochlorobenzene which melted at 65–66°.

The original fractions boiling above 168° were combined and distilled through the Fenske column. There were obtained the following fractions: 2 g. at 170–180°, 6.8 g. at 180–185°, 5.3 g. at 185–187.6°, 8.5 g. at 187.6–192°, 0.9 g. at 192–200° and a small residue. The known chloroxylenes boil from 186.6 to 191.5° and the dichlorotoluenes from 198–206°. It appeared probable that the methyl radical and not the chlorine had migrated. This conclusion was strengthened by the results of the determination of the density of the mixture of the two fractions which boiled between 187.6 and 192°; it was found to be 1.052²⁵. The density of 2,4-dichlorotoluene is 1.246²⁰,²⁰ and of 1,2-dimethyl-4-chlorobenzene is 1.069¹⁶,¹⁶. Since the densities of the isomers of these compounds differ but little, it is highly probable that the high-boiling fraction contained chloroxylenes.

Experiments with the Nitrotoluenes.—Equal molecular quantities of aluminum chloride and *o*, *m*, and *p*-nitrotoluenes were heated at 104° for two hours. The chloride dissolved and an oil was formed in each case. After decomposition with water a small amount of tar and the nitrotoluene used was recovered. When *p*-nitrotoluene was heated at 115, 125, and 150° for one hour the amount of tar was increased but no isomers were formed. Similar results were obtained when the meta compound was

heated at 115° for one hour. Tests for an amine in the products formed were negative. The result was not changed when 2 molecular quantities of aluminum chloride were used.

Summary

1. It was shown that when the chlorotoluenes are heated with aluminum chloride and hydrogen chloride rearrangement and disproportionation take place.

2. The extent to which these changes occur is determined by the temperature, time of heating and the molecular ratio of aluminum chloride to the chlorotoluene.

3. Under certain fixed conditions the stabilities of the isomers are ortho > meta > para.

4. Under certain conditions the mixture of the isomers obtained from *p*-chlorotoluene consisted of ortho, meta and para in the ratio 1–2–1.

5. Under the conditions used to cause the rearrangement of the chlorotoluenes, the isomeric nitrotoluenes and *p*-dimethylaminotoluene were not affected.

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The Rearrangement of the Xylenes by Aluminum Chloride

BY JAMES F. NORRIS AND GORDON T. VAALA¹

In certain Friedel and Crafts reactions in which a variety of substances are condensed with alkyl derivatives of benzene, the orientation of the alkyl groups in the products obtained is not the same as that in the hydrocarbons from which they were produced. Much work has been done on the rearrangement and disproportionation of such hydrocarbons, but the conditions used have been such that the results cannot be taken as a guide in Friedel and Crafts reactions, when it is desired either to avoid or to take advantage of the rearrangement. The isomeric xylenes were of particular interest because it was found that under certain conditions the chief product of the methylation of benzene was 1,2,4-trimethylbenzene and under other conditions a high yield of 1,3,5-trimethylbenzene was formed.² It appeared proba-

ble that xylenes were intermediate products. It was important to determine, if possible, whether the change in conditions led primarily to different orientation or to secondary rearrangements. In the earlier work it was shown that the three xylenes underwent appreciable rearrangement when they were heated with aluminum chloride at 55° for ten minutes.

This paper contains the results of a detailed study of the rearrangement of the xylenes. The following factors were investigated: the time, the temperature, the molecular ratio of hydrocarbon to aluminum chloride, the effect of the presence of varying amounts of ferric chloride, and the presence or absence of hydrogen chloride. The results were such that they have been of value in the control of several Friedel and Crafts condensations, which will be described in papers to be published later.

In determining the percentages of the three

(1) From the thesis of Gordon T. Vaala, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1936.

(2) Norris and Rubinstein, *THIS JOURNAL*, **61**, 1183 (1939).

isomers in the rearranged product, the freezing point method of Norris and Rubinstein was used for *p*-xylene. An improved apparatus was used, which facilitated the work and has been used in other investigations. The freezing point method when applied to *o*-xylene involved work at inconveniently low temperatures. A method of analysis based on oxidation of the mixture of the xylenes was developed and tested with synthetic mixtures. It was shown that the corresponding dibasic acids could be determined with an accuracy of about 90%.

The results of the experiments are given in the form of tables.

TABLE I

REARRANGEMENT OF *m*-XYLENE AT 50° IN THE PRESENCE OF HYDROGEN CHLORIDE

Mole ratio $1C_6H_4(CH_3)_2$ to $1AlCl_3$. The hydrocarbon used boiled at 139.2–139.5° and was shown by analysis to contain 1% *p*-xylene and less than 1% *o*-xylene.

Time, hours	Weight xylene used, g.	% re-covered hydrocarbons	% xylenes in recovered hydrocarbons	% isomers in recovered xylenes		
				Ortho	Meta	Para
0.5	85	92	100	3
1.5	65	94	100	16	77	7
5	53	95	88	14	74	12
18	85	95	85	16	69	15
30	43	93	84	16	69	15
48	43	87	80	16	67	17
75	43	89	72	16	65	19

TABLE II

REARRANGEMENT OF THE XYLENES IN THE PRESENCE OF HYDROGEN CHLORIDE

Mole Ratio $1C_6H_4(CH_3)_2$ to $1AlCl_3$

Xylene	Temp., °C.	Time	% xylenes in recovered hydrocarbons	% isomers in recovered xylenes		
				Ortho	Meta	Para
Ortho	50	5 hrs.	94	40	55	5
Meta	50	5 hrs.	88	14	74	12
Para	50	5 hrs.	83	14	76	10
Ortho	94	15 min.	84	38	46	16
Meta	94	15 min.	100	18	72	10
Para	94	15 min.	90	16	31	53

A comparison of the results in Table II with those of Norris and Rubinstein shows that at 55° for ten minutes the para isomer gave 3.4 times as much rearranged products as did the ortho; at

TABLE III

EFFECT OF MOLECULAR RATIO OF HYDROCARBON TO ALUMINUM CHLORIDE ON REARRANGEMENT OF *m*-XYLENE AT 50° IN THE PRESENCE OF HYDROGEN CHLORIDE

Moles xylene to moles $AlCl_3$	Time, hours	% xylenes in recovered hydrocarbons	% isomers in recovered xylenes		
			Ortho	Meta	Para
1	48	80	16	67	17
5	50	90	13	68	19
100	50	100	4

TABLE IV

EFFECT OF FERRIC CHLORIDE ON THE REARRANGEMENT OF *m*-XYLENE AT 50° FOR 20 HOURS IN THE PRESENCE OF HYDROGEN CHLORIDE

1 mole xylene ratio moles $AlCl_3$ to $FeCl_3$	% isomers in recovered xylenes		
	Ortho	Meta	Para
1 to 0	16	69	15
1 to 0.03	16	69	15
0.5 to 0.5	17	68	15

TABLE V

EFFECT OF HYDROGEN CHLORIDE ON THE REARRANGEMENT OF *m*-XYLENE AT 50° FOR 50 HOURS
Mole ratio 1 xylene to $1AlCl_3$

	% xylenes in recovered hydrocarbons	% isomers in recovered xylenes		
		Ortho	Meta	Para
With HCl	80	16	67	17
No HCl	96	14	71	15

50° for five hours 1.5 times, and at 94° for fifteen minutes 0.75 times. The percentage rearrangements of *m*-xylene under the two conditions used were approximately the same.

The conclusions from the results of the investigation can be used in the preparation of compounds by the Friedel and Crafts reaction and be used as a guide in the discovery of the structure of the compounds obtained. They furnish an explanation of the formation of pseudocumene when benzene is methylated at 0°; the orientation is ortho and para, as might be expected. At 100° the chief product is mesitylene in which the orientation is meta. In the simultaneous acylation and methylation of benzene by esters which is carried out best at about 100°, the orientation of the alkyl groups is largely meta.

A preliminary experiment has been made on the rearrangement of commercial pseudocumene with the thought that the reaction might be used as a convenient and cheap way of preparing mesitylene. A sample of pseudocumene (b. p. 169–171°) which was analyzed by sulfonation and found to contain 8.5% mesitylene, was heated with 2 moles of aluminum chloride at 94° for one hour. The recovered mixture of hydrocarbons contained 18% of mesitylene.

The fact that aluminum chloride produced a rearrangement of the xylenes led to a study of the condensation of methyl alcohol with pure *m*-xylene. The molecular ratios were 1.25 hydrocarbon, 0.25 methyl alcohol, and 0.75 aluminum chloride, the time five hours and temperature 110°; the yield of mesitylene boiling at 163.8° to 165.2° was 84%. After sulfonation and hydrolysis the yield was 80% of mesitylene which boiled

at 164–164.8° and gave a yield of 99.5% of the tribromo derivative which melted at 224–225° before crystallization.

A similar experiment was carried out but the time of heating was reduced to one and one-half hours and dry air was passed through the reacting mixture to remove the hydrogen chloride. In this case the yield of mesitylene boiling at 164.2–164.8° after sulfonation was 90% of the theoretical. With technical xylene at 90° for five hours, the yield of mesitylene was 34% and that of pseudo-cumene 37%.

Experimental

Details of an Experiment.—The aluminum chloride was placed in a 500-cc. round-bottomed flask fitted with a spiral return condenser, a motor-driven stirrer and a tube, leading to the bottom of the flask, through which dry hydrogen chloride was passed (1 bubble in two seconds). This tube contained a T through which the hydrocarbon could be introduced from an attached separatory funnel. The flask was heated in an oil-bath at the desired temperature, and the hydrocarbon, previously heated, was introduced. At the end of the desired time the product was cooled rapidly, decomposed by ice and hydrochloric acid in a flask, and distilled with steam. In certain experiments hydrogen chloride was not passed through the reactants.

Merck reagent anhydrous aluminum chloride was used in all experiments. The *m*-xylene was furnished by the du Pont Company. All temperatures are corrected; they were determined with a calibrated thermometer graduated in 0.2°.

Analytical Methods.—After the hydrocarbon had been heated with aluminum chloride the product was decomposed by ice and hydrochloric acid and distilled with steam. The weights of hydrocarbon used and of the mixture which distilled gave data for the percentage of hydrocarbon recovered.

The product was dried, distilled slowly through a 13-turn Davis column,³ and the temperature observed on a calibrated Anschütz thermometer with graduations of 0.2°. The material was collected in three fractions: I up to 137°; II 137–144°; III above 144°. The residue in the flask was redistilled in a 10-cc. flask and any material boiling at 137–144° was added to fraction II and higher boiling material, to fraction III. The sum of the weights of fractions I and III and the weight of fraction II were used in calculating percentage recovered xylenes.

Quantitative Determination of *p*-Xylene.—The lowering of the freezing point of pure *p*-xylene produced by a sample of the mixture gave data for calculating the percentage of compounds other than *p*-xylene in the mixture. The solvent was prepared from Eastman Kodak Co. pure *p*-xylene by distillation through a 13-turn Davis column; the fraction used boiled at 137.5–137.6° and melted at 13.0°. The freezing point constant was determined with toluene (b. p. 110.4–110.5°) and found to be 42.5 (value in literature, 43). The method was tested by analyzing

two known mixtures which contained I 8% para, 10% ortho, and 82% meta xylenes, and II 20% para and 80% meta xylenes. Mixture I was found to contain 8.3% and mixture II 20.4% *p*-xylene.

In determining freezing points, a very convenient modification of the Hortvet cryoscope⁴ was used. The apparatus consisted of a tall 1-liter vacuum bottle, insulated with a metal case and covered with a tightly fitting cork with a central opening for a metal tube 4 cm. in diameter and 20 cm. long. This tube served as an air jacket for a test-tube (18 × 2.5 cm.) which was fitted to it by a cork. The cooling was accomplished by passing dry air through a 4-mm. metal tube which extended to the bottom of the vacuum bottle where 500 cc. of ether had been placed. The tube ended in a loop which was pierced with pin holes to permit the formation of a stream of air bubbles. The evaporation of the ether produced by drawing air through it caused a lowering of the temperature which could be held within 0.10° at temperatures from 20 to –10°. In making the freezing point determinations the bath was held at 8 ± 0.1°, and the solution was supercooled about 0.3°. Determinations checked within 2%.

Quantitative Determination of *o*-Xylene.—A method was developed for the oxidation of the three xylenes to the corresponding phthalic acids, which gave sufficiently high yields to make the method useful for quantitative determinations. *o*-Xylene gave 89.4% of an acid which was shown by titration to be 98.6% dibasic; the corresponding figures with *p*-xylene were 88.3 and 97.4% and with *m*-xylene 91.3 and 98%.

The method was as follows: 4 cc. of the xylene, measured in a calibrated pipet, was placed in a 500-cc. flask fitted with a motor-driven stirrer through a mercury seal, a reflux spiral condenser, and a dropping funnel. The flask was heated to 120° and 3.8 cc. of bromine added drop by drop. Next, 10 cc. of a saturated solution of sodium hydroxide diluted with an equal volume of water was added. After the solution was refluxed for one hour, 100 cc. of a 5% solution of potassium permanganate (one-third the theoretical amount) was added. After heating for fifteen minutes, another 100 cc. was added and after one hour, 130 cc. The total time of refluxing was six hours. The cooled solution was treated with sulfur dioxide and filtered. The filtrate and washings from manganese dioxide were concentrated to about 150 cc. and poured into a 25% excess of concentrated hydrochloric acid. In a few minutes the hot solution was filtered; the precipitated isophthalic and terephthalic acids were washed with cold water, dried, and weighed. The filtrate and washings were evaporated to dryness, the residue powdered and transferred to a 500-cc. round flask with a long neck. Into the latter was placed a test-tube through which water flowed. The flask, surrounded and covered by asbestos, was placed on an iron gauze and asbestos and heated by a flame to such a temperature that a thermometer placed in the jacket just above the gauze registered 180–190°; the phthalic anhydride sublimed slowly. At the end of from two to three hours the anhydride collected as a compact crystalline mass on the cooled test-tube. The latter was withdrawn, the

(3) H. S. Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 81 (1929).

(4) Hortvet, *J. Ind. Eng. Chem.*, **13**, 203 (1921).

anhydride dissolved in 200 cc. of neutral alcohol and titrated with 0.1 *N* sodium hydroxide solution. To test the purity of the acid it was recovered and converted into phthalic anhydride. The quantitative isolation of the anhydride in this way was tested with a weighed sample which was converted into the salt, liberated and sublimed, and titrated. The recovery was 95.7%. In a second test a mixture of 1 g. each of the three phthalic acids gave a recovery of *o*-phthalic acid of 97%.

We were unable to find a quantitative method for the separation of isophthalic and terephthalic acids. As a consequence, the percentage of *m*-xylenes in the mixtures analyzed was considered to be the difference between the weights of the mixed xylenes and the sum of the ortho and para isomers. In several experiments the weight of *m*-xylene was calculated from the weights of the *p*-xylene and of the isophthalic and terephthalic acids obtained. The result checked within less than 1% the value obtained.

Summary

1. The effect of aluminum chloride on the three xylenes was studied under different conditions.

2. It was found that (1) change in temperature affects the relative proportions in which the isomers are formed; (2) rearrangement takes place much more rapidly than the decomposition of the hydrocarbons and yields a mixture approaching that present in commercial xylene; (3) decrease in the molecular ratio of aluminum chloride decreases the rate of rearrangement and the percentage decomposition; (4) the presence of ferric chloride had little or no effect and (5) hydrogen chloride did not affect rearrangement but appeared to increase decomposition.

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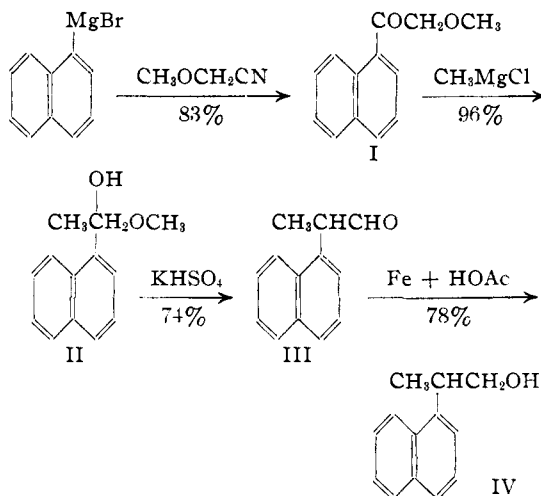
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Synthetic Experiments in the Chrysene Series

BY LOUIS F. FIESER, LLOYD M. JOSHEL¹ AND ARNOLD M. SELIGMAN^{2,3}

The goal of the present work was the development of a synthesis of 5-methylchrysene which would be capable of application as well to the synthesis of 4,5-dimethylchrysene, both hydrocarbons being desired as possible models of the carcinogenic 3,4-benzpyrene.⁴ The scheme selected for investigation required 2-(α -naphthyl)-propionaldehyde (III) as an essential intermediate, and a method for the preparation of the aldehyde was found which is very satisfactory for the case at hand and which should be capable of other applications. The remainder of the plan could not be realized, for a rearrangement was encountered in the final stages of the synthesis.

In the most satisfactory procedure for preparing the intermediate aldehyde, α -naphthylmagnesium bromide was condensed with methoxyacetone to give the keto ether I and this by interaction with methylmagnesium chloride was converted into the carbinol ether II in over-all yield of 80%. It is not practical to reverse the order of the two Grignard reactions, for when methylmagnesium chloride was added to methoxyacetone ac-



ording to Gauthier⁵ and the resulting methoxyacetone condensed with α -naphthyl Grignard reagent, the over-all yield of II was only 12%. Carbinol ethers analogous to II have been synthesized similarly by Bradsher and Schneider⁶ from 2-iodobiphenyl and cyclized with acids to phenanthrene derivatives. Our methyl-methoxy-methyl- α -naphthylcarbinol (II) in the next step was distilled over potassium bisulfate, when methyl alcohol was liberated and the chief product was 2-(α -naphthyl)-propionaldehyde (III). This

(1) Fellow of the Finney-Howell Research Foundation.

(2) George Cheyne Shattuck Memorial Fellow and Jeffries Wyman Scholar of the Harvard Medical School.

(3) The procedures for the synthesis of 2-(α -naphthyl)-propionaldehyde and the corresponding alcohol were worked out originally by A. M. Seligman and the further experiments were all conducted by Dr. L. M. Joshel.

(4) Fieser and Seligman, *THIS JOURNAL*, **60**, 170 (1938).

(5) Gauthier, *Ann. chim.*, [8] **16**, 318 (1909).

(6) Bradsher and Schneider, *THIS JOURNAL*, **60**, 2960 (1938).