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The Rearrangement of Certain Derivatives of Toluene by the Action of Aluminum Chloride

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Many investigations have shown that derivatives of benzene which contain only alkyl groups undergo disproportionation and rearrangement when heated with aluminum chloride. We have not found reports of any study of the rearrangement of alkyl groups in aromatic compounds which contain, in addition to these groups, an atom or group of a different type. The influence of the nature of a substituent on the reactivity of a particular atom or group in a compound has been studied for several years in this Laboratory and it was of interest to extend the study to include the influence of different classes of substituents on the change of position of an alkyl group brought about by the action of aluminum chloride. Further, if rearrangement took place the process might be used as a means of preparing from a readily accessible compound an isomer which is formed to a small extent during nitration, chlorination, etc. For example, if *m*-chlorotoluene or *m*-cresol could be formed from their isomers, the method might make available compounds which are now obtained by indirect methods.

In this paper are described the results of the study of heating with aluminum chloride the following: *o*-, *m*- and *p*-chlorotoluene, *o*-, *m*-, and *p*-nitrotoluene, *p*-cresol, and *p*-dimethylaminotoluene. The effects of change in temperature, time, and the molecular ratio of the aluminum chloride to the second reactant were studied in certain cases. Appreciable rearrangement was observed only with the chlorotoluenes and *p*-cresol. The addition compounds formed from the amines and aluminum chloride were stable at the temperatures used. In the case of the limited number of compounds studied, it appears that the ortho and para orienting groups methyl, hydroxyl, and chlorine produce in a methyl radical sufficient reactivity to permit a change of position of the latter in the molecule. The meta orienting nitro group stabilizes a methyl radical so that it does not migrate under the conditions that affect the other class of compounds.

p-Chlorotoluene was studied first because a preliminary experiment showed that it underwent both rearrangement and disproportionation and resembled *p*-xylene in its behavior. The products resulting from disproportionation indicated that the methyl radical and not the chlorine atom was involved in the change. It has been shown that bromobenzene, when heated at its boiling point with aluminum chloride, yields benzene and *p*-dibromobenzene,² but the conditions used in our experiment were much less drastic.

The main difficulty to be overcome in the case of the chlorotoluenes was the quantitative determination of the amount of each isomer in the rearranged product. After the investigation of chemical procedures, which proved to be inadequate, a physico-chemical method was adopted. The amount of the para compound in the mixture, which contained only the isomers, was determined by the freezing point lowering of *p*-chlorotoluene produced by the mixture; this was a measure of the sum of the *o*- and *m*-chlorotoluenes present. A modified form of the Swietoslawski differential ebullioscope³ was used to determine the percentages of the ortho and of the meta compounds in the mixture. The temperature of the vapor from a rapidly boiling mixture which contained a fixed percentage of the para isomer was determined, and its position on a plot previously prepared was noted. This plot was made by determining the temperature of the vapor of a series of mixtures which contained a definite percentage of the para compound and varying percentages of the other isomers. The change in vapor temperature with change in composition was sufficient to give results accurate within a few per cent. The results are given in the table.

An examination of the table leads to the following conclusions: (a) *p*-chlorotoluene undergoes rapidly both rearrangement and disproportionation when heated with aluminum chloride at 100°; (b) from expts. 1 and 2 it is seen that when heated for half an hour a large change in the molecular

(1) From the thesis of Howard S. Turner presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1936.

(2) Dumreicher, *Ber.*, **15**, 1867 (1882); Coposarow, *J. Chem. Soc.*, **119**, 442 (1921).

(3) M. W. Swietoslawski, *Bull. soc. chim.*, **49**, 1567 (1931) (Fig. 4).

TABLE I

REARRANGEMENT OF CHLOROTOLUENES BY ALUMINUM CHLORIDE IN THE PRESENCE OF HYDROGEN CHLORIDE

In each experiment 16 g. of chlorotoluene was used. Experiments 1-10 refer to the para compound; in experiment 11 the meta and in experiment 12 the ortho compounds were used.

Expt.	Mole ratio CH ₃ C ₆ H ₄ - Cl to AlCl ₃	Time, hours	Temp., °C.	G. from final distn.	Wt. % of I up to 158°	% of fractions in prod. II 158° to 163°	III residue	% re- arranged prods. in fraction II	% recov. prods. other than chloro- toluenes	% compn. of fraction II Ortho	Meta	Para
1	1	0.5	100	12.9	8.5	68.3	23.2	41.8	31.7	21.5	20.3	58.2
2	10	.5	100	13.4	6.7	71.6	21.7	36.5	27.4			63.5
3	1	4	100	12.5	35.2	32.8	32.6	85.8	67.2	50.4	35.4	14.2
4	10	4	100	14.2	13.9	65.2	20.9	74.7	34.8	30.2	44.5	25.3
5	10	36.5	50	14.5	5.5	69.7	24.8	23.4	30.3			76.6
6	1	2.5	100	12.2	24.0	45.0	33.0	80.6	55.0			19.4
7	10	36.5	70	10.2	23.4	40.0	36.2	64.3	60.0			35.7
8	10	72	54	14	15.5	60.2	20.9	53.9	39.8			46.1
9	1	36.5	55	14	10.9	65.5	23.6	67.8	34.5	29.3	38.5	32.2
10 Para	10	4.25	96	14.5	18.3	56.8	24.9	73.4	43.2	24.8	48.6	26.6
11 Meta	10	4.25	96	14.5	9.4	77.5	13.1	50.8	22.5	32.9	49.2	17.9
12 Ortho	10	4.25	96	15	8.9	83.4	7.7	21.6	16.6	78.4	17.1	4.5

The figures in the column headed "% recovered products other than chlorotoluenes" were calculated from the weights of fractions I, II and III. It is probable that small amounts of the chlorotoluenes were not separated from fractions I and III; for this reason the values of the percentages of recovered products other than chlorotoluenes are presumably too great. The results are comparable, however.

ratio of the chlorotoluene to aluminum chloride has little effect, whereas in four hours the larger proportion of aluminum chloride produced a much greater increase in disproportionation than in rearrangement. This difference also was observed in the case of the xylenes⁴; (c) it is seen from expts. 1, 6 and 3 (mole ratio 1:1) that increase in time results in approximately equivalent increases in the amounts of both rearrangement and disproportion. When less aluminum chloride was used in expts. 2 and 4 (mole ratio 10 to 1) increase in time produced a much larger increase in rearrangement than in disproportionation; (d) increase in temperature (expts. 5 and 7) from 50 to 70° doubled the disproportionation and increased rearrangement 2.8 times; (e) of the three isomers (expts. 10, 11 and 12) the ortho is the most stable under the conditions used; the para is the least stable. Of the original isomer in the rearranged product the ortho compound yielded 78.4%, the meta 49.2% and the para 26.6%. It would be possible to prepare *m*-chlorotoluene from the para compound.

Attempts made to produce rearrangements of the three nitrotoluenes by aluminum chloride and hydrogen chloride were unsuccessful. The temperature used varied from 100 to 150°, the time from half an hour to two hours and the molecular ratios of aluminum chloride to nitro compound were 1 to 1 and 2 to 1. At the lower temperature the nitro compound was recovered unchanged;

at the higher temperatures tars were formed.

Since there was such a marked difference between the activating influence of a chlorine atom and a nitro group on a methyl radical joined to a benzene ring, it appeared desirable to study the influence of a dimethylamino group. It has been shown⁵ that dimethylaniline is recovered unchanged after being heated at 250° for ten hours. The amine is converted into methyl chloride and aniline hydrochloride when heated with hydrogen chloride.⁶ These facts were considered in the experiments with *p*-dimethylaminotoluene. The compound of the latter with aluminum chloride in the absence or presence of hydrogen chloride was so stable that it suffered no appreciable change on heating.

A preliminary experiment has been made with *p*-cresol. When the compound (0.19 mole) was heated at 200° for one and one-half hours with aluminum chloride (0.38 mole), rearrangement took place. The meta isomer which was formed in appreciable quantities was identified by the melting point of the trinitro derivative.

Experimental

Details of an Experiment.—The apparatus used in most of the experiments consisted of a round-bottomed flask provided with an inlet tube through which hydrogen chloride (1 to 2 bubbles per sec.) was passed, a mechanically driven stirrer and a reflux condenser fitted with a calcium chloride tube. The flask containing the reactants was placed in a glycerol bath which was heated by a

(5) Giraud, *Bull. soc. chim.*, [3] 1, 691 (1888).

(6) Lauth, *Ber.*, 6, 677 (1873).

(4) Norris and Vaala, *THIS JOURNAL*, 61, 2131 (1939).

refluxing liquid for the desired time. There appeared to be little or no solution of the aluminum chloride in the chlorotoluene. The mixture was treated with ice and hydrochloric acid and distilled with steam. In certain cases the separation of the organic liquid was difficult. If a partial emulsion was formed this was separated, and treated with a little water and calcium chloride. The dense aqueous solution helped in the separation of the two liquids. The product was dried with calcium chloride and distilled very slowly through a 13-turn Davis column.

Compounds Used.—The *p*-chlorotoluene was made from *p*-toluidine and distilled through a 12-turn Davis column; a cooling curve showed that it melted at 7.2° (6.2 to 7.5° in the literature). The ortho and para compounds obtained from the Eastman Kodak Company were fractionated with the Davis column⁷; the ortho isomer was collected at 158.7–158.9° at 754 mm. (literature 159.15 at 760 mm.); the meta compound boiled at 161.8–162° at 768 mm.

The nitrotoluenes were obtained from the Eastman Kodak Company; the para compound melted at 51–53°; the meta at 15–16°; and ortho at –6°. The *p*-dimethylaminotoluene (Kahlbaum) melted at –30.5° (thermometer not calibrated). The *p*-cresol (Eastman Kodak Company) melted at 32.5° (literature 33.5°). Merck pure sublimed aluminum chloride was used.

Methods of Analysis for the Chlorotoluenes.—The amount of the para compound in a mixture containing only the three isomers was found by determining the lowering of the freezing point of pure *p*-chlorotoluene produced by the mixture. The freezing point constant for *p*-chlorotoluene was determined by using *m*-chlorotoluene as solute; two determinations gave 5.92 and 5.97 as the constant. The determinations were made in the apparatus previously described.⁴ The method was tested by the analysis of a mixture of known composition, para 50%, meta 33.3%, ortho 16.7%; found 47.8 and 49.8% para.

The determinations of the amounts of the ortho and the para isomers in the mixtures were made in a Swietoslawski differential ebullioscope a drawing of which is included in the reference already given. The apparatus is designed to record the temperature of a boiling liquid and that of the vapor from the liquid, which is condensed and returned to the flask in which the liquid is boiling. Tests of the apparatus designed with a boiling flask of 5-cc. capacity showed that the temperatures of the vapor could be reproduced more accurately than those of the liquid; as a consequence the vapor temperatures were used in the determinations. The apparatus was heavily insulated by cork. In order to operate at a constant and reproducible pressure, the end of the reflux condenser was connected with a 5-gallon (20-liter) bottle which contained 5 lb. (2.5 kg.) of calcium chloride to keep the air at a constant content of moisture. The bottle was placed up to its neck in a large container filled with water. The bottle was connected to a 1-liter flask kept in a thermostat. When a determination was to be made the pressure in the apparatus was adjusted so that the surfaces of the mercury in the two arms of the manometer were at the same level. This arrangement kept the pressure so nearly

constant that the temperatures of the vapor during an experiment varied less than 0.005°. In duplicate determinations the temperatures checked within 0.01°.

With this apparatus the temperatures of the vapor from mixtures of varying composition of the three isomers were determined. In each case 11 g. of the mixture which contained 9 g. of the para isomer was used; the amounts of ortho and meta isomers were varied from 2 g. ortho and 0 g. meta to 0 g. ortho—2 g. meta. Determinations on eleven mixtures gave data for a curve that deviated only slightly from a straight line. The difference in the temperatures of the vapors from the two mixtures which varied most in composition was 0.52°. In each case five observations at different time intervals were made of the temperature of the vapor, and the values were averaged. The difference between the several single observations in the case of a particular mixture varied from 0.001 to 0.004°. An analysis was made of a mixture of known composition: calcd., *o* 16.7%, *m* 33.3%, *p* 50%; found, *o* 15.2%, *m* 34.8%, and *p* 48.8%.

In the analyses of the mixtures produced by rearrangement, the product obtained as the result of heating the chlorotoluene with aluminum chloride was distilled with steam and the volatile material was weighed. After drying, the mixture was distilled very slowly through a 12-turn Davis column and separated into three fractions: I up to 158°, II 158–163°, III residue. The percentage of the para isomer in fraction II was next determined. The weight of the mixture that contained 2 g. of the ortho and para compounds was calculated, weighed and taken for analysis. The weight of the para isomer in this sample was calculated and enough of the para compound was added so that the resulting mixture contained 9 g. of para and 2 g. of a mixture of ortho and meta chlorotoluenes. The temperature of the vapor from this mixture when it was boiled in the ebullioscope was determined as before. The position of the temperature on the plot gave the percentages of the ortho and of the meta compounds in the mixture.

An experiment was made with *p*-chlorotoluenes to determine to what extent a more careful fractionation of the mixture before analysis would affect the percentages of the isomer in the fraction boiling at 158–163°. The three fractions obtained with the Davis column were refractionated through a Fenske column⁸ (15 theoretical plates). The analyses of the fraction boiling between 158 and 163° showed that the product of the first distillation contained 75.2% of the ortho and meta isomers and after the second distillation 80.6%. As a result of the second distillation the weights of the first and third fractions decreased and the middle fraction increased. As stated in the note in the table the percentages of disproportion given are too great. We were particularly interested in rearrangement and did not carry out the additional fractionation on the experiments reported.

In order to determine what products had been formed as the result of disproportionation, the low boiling fractions from all the experiments were combined and fractionated through a Fenske column equivalent to 13 theoretical plates. About 75% of the material boiled

(7) H. S. Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

(8) M. R. Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

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 and of 1,2-dimethyl-4-chlorobenzene is 1.069¹⁵. 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

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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**, 1163 (1939).