Resolution and Racemization of N-Carboxymethyl-N-methyl-3-bromomesidine.—A chloroform solution of 3.10 g. of N-carboxymethyl-N-methyl-3-bromomesidine and 3.20 g. of cinchonidine was evaporated *in vacuo* from 100 ml. to approximately 10 ml. The viscous residue was dissolved in 150 ml. of acetone by boiling under reflux for one hour. When the filtered acetone solution was allowed to stand overnight in a refrigerator, a colorless solid formed, which was removed by filtration and stored in a refrigerator. More solid crystallized out, as the solution stood at low temperature. Four crops were collected totaling in weight about 90% of the salt present; the melting point and rotation of each was essentially the same.

Crop	Time, days	Wt., g.	$[\alpha]^{33}\text{D}$	M.p., °C.
1	1	2.995	−56.3°	157–158
2	2	1.229	−58.0	158–158.5
3	3	0.403	−57.2	157–158
4	6	0.995	−57.5	156–158

Anal. Calcd. for $C_{12}H_{16}BrNO_2 \cdot C_{19}H_{22}N_2O$: C, 64.13; H, 6.60. Found: C, 64.11; H, 6.78.

By repeated extraction of combined crops 1 and 2 with 20% aqueous hydrochloric acid to which ice was added, 1.5 g. of *d*-acid was isolated, m.p. 104–104.5°.

From 1.25 g. of the *d*-acid, 20 ml. of a solution in methyl acetate was prepared, which was used in racemization experiments at the temperature of boiling methyl acetate (57°). The previously described technique with sealed tubes[22] was employed.

The results of one run, which were very closely duplicated in a second run, were as follows: 0.0 hr., αD +0.661°, $[\alpha]^{33}\text{D}$ +10.8°; 0.25 hr., αD +0.417°, $[\alpha]^{33}\text{D}$ +6.82°; 0.5 hr., αD +0.269°, $[\alpha]^{33}\text{D}$ +4.40°; 0.75 hr., αD +0.166°, $[\alpha]^{33}\text{D}$ +2.72°; 1.0 hr., αD +0.116°, $[\alpha]^{33}\text{D}$ +1.90°; 1.5 hr., αD +0.032°, $[\alpha]^{33}\text{D}$ +0.8°. From these data, $t_{1/2}$ = 0.47 hr.

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[22] R. Adams and K. V. Y. Sundstrom, THIS JOURNAL, **76**, 5474 (1954).

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[CONTRIBUTION NO. T203, FROM THE RESEARCH LABORATORY, THE GOODYEAR TIRE AND RUBBER COMPANY]

The Chloromethylation of Toluene and Conversion of *p*-Xylyl Chloride to Terephthaloyl Chloride

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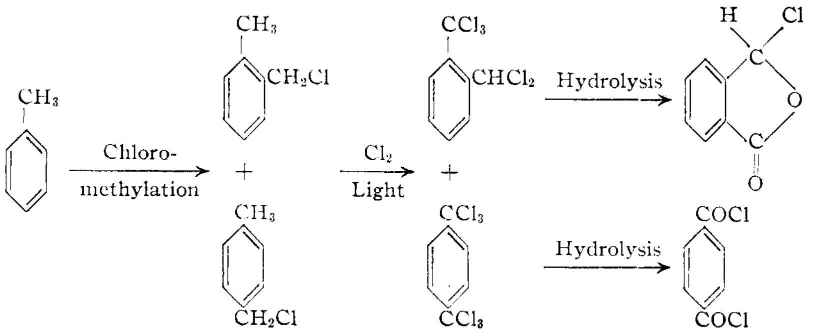
RECEIVED MAY 1, 1954

A study has been made of the chloromethylation of toluene, and a viscosimetric method has been developed for the determination of the percentages of isomers present in the reaction products. The mixtures of *o*- and *p*-xylyl chlorides (α-chloro-*o*-xylene and α-chloro-*p*-xylene) have been chlorinated in the side chains and it has been shown that hexachloro-*p*-xylene (α,α,α,α′,α′,α′-hexachloro-*p*-xylene) can be separated from the mixtures. Hexachloro-*p*-xylene has been converted to terephthaloyl chloride in high yields by means of hydrolysis with maleic acid.

The need for relatively large quantities of terephthaloyl chloride suggested that it might be obtained economically from toluene. The present investigation describes studies of the chloromethylation of toluene, chlorination of the resulting reaction products, separation of the mixtures of pentachloro-*o*-xylene (α,α,α,α′,α′-pentachloro-*o*-xylene) and hexachloro-*p*-xylene and hydrolysis of the latter compounds to acid chlorides. The transformations involved may be summarized by means of the equations



Although earlier investigators indicated that the chloromethylation of monoalkyl benzenes leads principally to *para* chloromethyl derivatives, Hill and Short[2] have shown that the introduction of a chloromethyl group into toluene, by the use of dichloromethyl ether or paraformaldehyde, affords a considerable amount of *o*-xylyl chloride (53 and 42%, respectively). Recently, Brown and Nelson[3] determined the ratio of isomers in the product obtained by chloromethylation of toluene using trioxymethylene in acetic acid at 60° with hydrogen chloride and zinc chloride. They obtained values of 34.7, 1.3 and 64.0 for the percentage distribution of the *ortho, meta* and *para* isomers, respectively.

In an attempt to increase the ratio of *para* to *ortho* substitution, a relatively extensive series of chloromethylation reactions of toluene was carried out. Approximately equal amounts of the two isomers resulted on zinc chloride catalysis under a wide variety of conditions. Other catalysts such as ferric chloride, aluminum chloride, stannic chloride, sulfuric acid, phosphoric acid and boron trifluoride did not alter the ratios of isomers more than a few per cent.

The mixtures of *o*- and *p*-xylyl chlorides (b.p., 96–98° (25 mm.)) cannot be separated by conventional distillation. Since the procedure of Hill and Short[2] for the analysis of mixtures of *o*- and *p*-xylyl chlorides consists of hydrolyzing the mixture and carrying out a thermal analysis of the derived xylyl alcohols, it does not lend itself to a study of a large number of samples. Accordingly, a new method was sought for the determination of the percentages of isomers present in the various reaction mixtures. Since the study described here was completed several

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[1] Department of Chemistry, University of Missouri.

[2] P. Hill and W. F. Short, *J. Chem. Soc.*, 1123 (1935).

[3] H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

years ago, the analytical procedure of Brown and Nelson[3] was unknown at that time.

It was found that pure *o*- and *p*-xylyl chlorides differ considerably in their viscosities. Mixtures of known amounts of these compounds were prepared, and their times of flow plotted against composition to give a curve. The plot of reciprocal of time *vs.* composition leads essentially to a straight line as shown in Fig. 1. Analyses of the xylyl chloride mixtures were determined by reference to this graph. It was assumed that the amount of *m*-xylyl chloride present in the mixtures was low, and it is believed that the values obtained were accurate to about 4–5%.

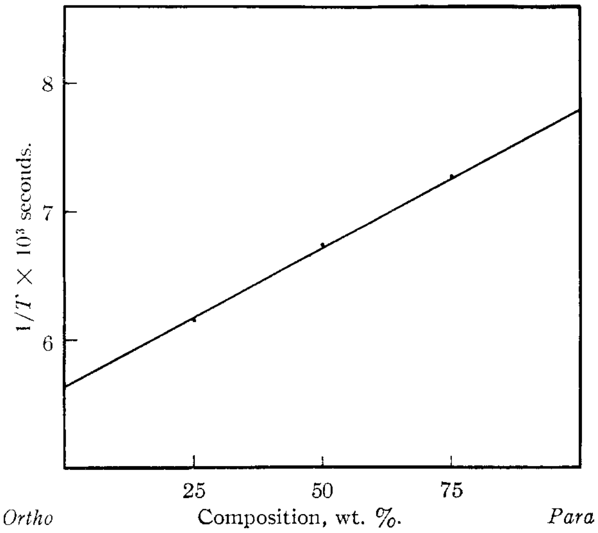

Fig. 1.—Viscosity relationship of *o*-xylyl chloride and *p*-xylyl chloride at 30°.

It is known[4] that the chlorination of *p*-xylene in the presence of light leads to hexachloro-*p*-xylene which is contaminated with relatively little nuclear chlorinated material. Under similar conditions, *o*-xylene gives pentachloro-*o*-xylene.[5] The chlorination of the mixtures of xylyl chlorides was accomplished readily to produce clean reaction products which apparently consisted of an approximately 50:50 mixture of hexachloro-*p*-xylene and pentachloro-*o*-xylene.

It was discovered that the hexachloro-*p*-xylene could be separated quite readily from the crude reaction mixtures in relatively high yields (80–85%) and a good state of purity. The oily residue which remained after removing the hexachloro-*p*-xylene contained principally pentachloro-*o*-xylene contaminated with a few per cent. of the hexachloro compound. No attempt was made to isolate the pentachloro-*o*-xylene in pure form; however, hydrolysis studies were carried out on the impure material as described below.

Mills[6] has demonstrated that benzotrichloride can be caused to react with aliphatic acids in the presence of certain acid catalysts to give benzoyl chloride and the corresponding aliphatic acid chlorides. Attempts to convert hexachloro-*p*-xylene to terephthaloyl chloride by reaction with acetic acid gave low yields of acid chlorides under the conditions employed. Phthalic and succinic acids effected the conversion of hexachloro-*p*-xylene to terephthaloyl chloride and the corresponding anhydrides in fair yields; however, difficulties were encountered in separating the desired product from the anhydrides. The boiling point of maleic anhydride appeared to offer the possibility of separating this material from terephthaloyl chloride by means of distillation. This indeed was found to be true and the conversion of hexachloro-*p*-xylene to terephthaloyl chloride was accomplished in yields of the order of 90% by the use of maleic acid in the presence of a catalyst such as zinc chloride.

The complete hydrolysis of mixtures of hexachloro-*p*-xylene and pentachloro-*o*-xylene by means of a water solution of acetic and sulfuric acids produced a separable mixture of terephthalic and phthalaldehydic acids. Controlled hydrolysis of the mixture of chloro compounds led to a mixture of terephthaloyl chloride and 3-chlorophthalide. A similar hydrolysis of pure pentachloro-*o*-xylene gave 3-chlorophthalide in fair yield.

Acknowledgment.—The author would like to thank P. J. Flory for suggesting the possibility of the viscosimetric approach to the determination of the compositions of the xylyl chloride mixtures. He also wishes to acknowledge the assistance of L. Wallen and Marcia C. Shaffer with some of the laboratory work. He is indebted to the Goodyear Tire and Rubber Company for permission to publish the results of this investigation.

Experimental

Chloromethylation of Toluene.—The materials employed for this study were obtained from commercial sources with the exception of *sym*-dichlorodimethyl ether which was synthesized according to the method of Stephen, Short and Gladding.[7] The following experiment is representative of the procedure which appeared to be the most practical for the preparation of mixed xylyl chlorides. In a 2-l., three-necked flask equipped with a mechanical stirrer, a reflux condenser, the top of which was connected to a gas-trap, and a gas inlet tube were placed 800 g. (8.6 moles) of toluene, 150 ml. (2 moles) of 40% formalin, 300 ml. of concentrated hydrochloric acid and 136 g. (1 mole) of anhydrous zinc chloride. The flask was placed in a water-bath, maintained at 60°, and the reaction mixture was stirred rapidly while anhydrous hydrogen chloride was introduced for a total of 12 hours. The layers were separated and the toluene solution was washed twice with water, once with 10% sodium bicarbonate solution and twice more with water. After drying over calcium chloride, the excess toluene was removed on a steam-bath under reduced pressure and the residue was distilled *in vacuo* through a 20″ packed column. There was obtained 248 g. (88%) of mixed xylyl chlorides which boiled at 96–98° (25 mm.). The residue weighed 16 g.

Preparation of *o*- and *p*-Xylyl Chlorides.—These compounds were obtained by treating *o*- and *p*-xylene (Eastman Kodak Co. best grade) with sulfuryl chloride according to the method of Kharasch and Brown.[8] They had the following physical properties: *o*-xylyl chloride, b.p. 95–96° (25 mm.), $n^{20}D$ 1.5391; *p*-xylyl chloride, b.p. 96–97° (25 mm.),

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(4) P. Osswald and O. Scherer, U. S. Patent 2,132,361; *C. A.*, **33**, 177 (1939).

(5) E. T. McBee, H. B. Hass, P. E. Weimer, G. M. Rothrock, R. M. Robb and A. R. van Dyken, Natl. Nuclear Energy Ser., Div. VII, **1**, Prepn., Properties, and Technol. of Fluorine and Org. Fluorine Compds., 207–221 (1951); *C. A.*, **46**, 2513 (1952).

(6) L. E. Mills, U. S. Patent 1,965,556; *C. A.*, **28**, 5474 (1934).

(7) H. Stephen, W. F. Short and G. Gladding, *J. Chem. Soc.*, **117**, 510 (1920).

(8) M. S. Kharasch and H. C. Brown, This Journal, **61**, 2142 (1939).

n^{20}D 1.5367. The viscosity data in Fig. 1 were determined at 30° in a No. 1 Ubbelohde viscometer.

Chlorination of the Mixture of *o*- and *p*-Xylyl Chlorides.—The following procedure is typical of a number of runs which were carried out. In a 5-l. three-necked, ground glass jointed flask, equipped with a condenser, gas inlet tube and thermometer well was placed 2710 g. of the mixed xylyl chlorides. The flask was heated by means of an electric mantle and a tube connected the top of the condenser with a gas trap. The flask was illuminated with a 150-watt electric light bulb which was placed within about $^1/_2$″ of the flask. The xylyl chlorides were heated to about 100°, and chlorine was introduced slowly near the bottom of the flask. The heating and rate of flow of chlorine were adjusted so that a temperature of 145–150° was maintained throughout the course of the reaction. The product weighed 5720 g. If it is assumed that the mixture contained equimolar amounts of hexachloro-*p*-xylene and pentachloro-*o*-xylene, the yield was essentially quantitative. Analyses for total and side-chain chlorine gave values of 66.72, 66.51 and 65.88, 65.99, respectively.

Separation of the Mixture of Hexachloro-*p*-xylene and Pentachloro-*o*-xylene. (a) **By Crystallization from Acetic Acid.**—A sample of 100 g. of the mixture was dissolved in 75 ml. of acetic acid by warming. Upon cooling to 10°, there was obtained 46.0 g. of hexachloro-*p*-xylene; m.p. 107–109°, lit.[9] m.p. 110°.

(b) **By Crystallization and Centrifugation.**—A sample of the chlorination product (5550 g.) was allowed to stand at room temperature for one day and partial crystallization occurred. The oil was decanted as completely as possible and the solid was centrifuged at a speed of 3,500 r.p.m. There was obtained 2500 g. of hexachloro-*p*-xylene, m.p. 107–110°. In some cases, the partially solidified chlorination product showed a tendency to undergo further crystallization upon being broken up and being transferred to the centrifuge. Such material melted below 100° after centrifugation; however, by warming it with an equal weight of methanol, cooling and filtering, hexachloro-*p*-xylene (m.p. 108–111°) could be obtained in yields comparable to those given by the preceding procedures.

Hydrolysis of Hexachloro-*p*-xylene to Terephthaloyl Chloride.—In a 2-l. three-necked flask equipped with an air-cooled condenser, mechanical stirrer and a tube for the addition of solids were placed 469.5 g. (1.5 moles) of hexachloro-*p*-xylene and 3.1 g. (0.5% by weight of total reactants) of anhydrous zinc chloride. The flask was heated in an oil-bath at 135–140°. When the contents of the flask had liquefied and come to temperature, the stirrer was started and 353 g. (3.04 moles) of maleic acid was added in small portions. The reaction was quite vigorous and was controlled by the rate of addition of the maleic acid. The large quantity of hydrogen chloride which was evolved was led from the top of the condenser to a gas absorption trap.

After all of the maleic acid had been added, a clear melt resulted. It was heated and stirred for an additional 5 minutes, allowed to cool to about 80° and decanted from the zinc chloride into a flask which was equipped with a 20″ helices-packed column with a wide-bore side-arm. The maleic anhydride was removed up to 85° (20 mm.), a small fraction was collected at 85–134° (20 mm.) and then 289 g. (95%) of terephthaloyl chloride distilled at 134–136° (12 mm.), m.p. 80–82°, lit.[10] m.p. 83–84°.

Hydrolysis Studies on the Mixture of Hexachloro-*p*-xylene and Pentachloro-*o*-xylene. (a).—A mixture of 1326 g. of the mixture of hexachloro-*p*-xylene and pentachloro-*o*-xylene and 1000 ml. of acetic acid was stirred and heated at reflux while a solution of 10 g. of sulfuric acid in 400 ml. of water was added dropwise. The reaction mixture was heated for about 40 hours, the precipitate was removed by filtration, washed with acetic acid, acetone and dried. The terephthalic acid weighed 393 g. The filtrate from the reaction mixture was treated with 15 g. of sodium hydroxide and concentrated under reduced pressure. The residue was crystallized from water and there was obtained 206 g. of phthalaldehydic acid, m.p. 94–96°, lit.[11] m.p. 95–96°.

(b).—A mixture of 591 g. of the hexachloro-*p*-xylene and pentachloro-*o*-xylene mixture and 5.3 g. (0.5% by weight of reactants) of anhydrous zinc chloride was stirred and heated at 135° while 470 g. of maleic acid was added in portions so that the evolution of hydrogen chloride was not too vigorous. After all of the maleic acid had been added, the reaction mixture was heated for an additional 30 minutes, allowed to cool to about 80° and decanted. The material was distilled through a short, packed column and after removal of the maleic anhydride, a fraction (300 g.) was collected at 140–144° (10 mm.). This was refractionated through a 30″ helices-packed column to give 130 g. of a product, b.p., 134–137° (10 mm.) and 105 g. material which boiled at 137–144° (10 mm.). The former melted at 77–80° after crystallization from cyclohexane and was impure terephthaloyl chloride. The higher boiling fraction was a mixture which contained terephthaloyl chloride and 3-chlorophthalide. The presence of the latter was indicated by oxidation of a sample of the mixture with alkaline permanganate solution to phthalic acid.

Preparation of 3-Chlorophthalide.—A mixture of 128 g. (0.46 mole) of pentachloro-*o*-xylene (obtained by chlorinating pure *o*-xylene) and 1.5 g. of anhydrous zinc chloride was heated and stirred at 135° while 110 g. (0.95 mole) of maleic acid was added in portions. The reaction mixture was heated for an additional 15 minutes, allowed to cool to about 80° and decanted into a distillation apparatus. After removal of the maleic anhydride and intermediate fraction, there was obtained 26 g. (34%) of 3-chlorophthalide which boiled at 149–150° (10 mm.), m.p. 60–61° (after crystallization from hexane), lit.[12] m.p. 61°.

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(9) A. Colson and H. Gautier, *Bull. soc. chim.*, [2] **45**, 507 (1886).

(10) C. Liebermann and M. Kardos, *Ber.*, **46**, 198 (1913).

(11) R. L. Shriner and F. J. Wolf, *Org. Syntheses*, **23**, 74 (1943).

(12) S. Gabriel, *Ber.*, **49**, 1608 (1916).