

## PREPARATION OF M-XYLYL CHLORIDE.

HAROLD S. KING and MARY K. MERRIAM.

Dept. of Chemistry, Dalhousie Univ., Halifax, N. S.

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## ABSTRACT.

Meta-xylene was chlorinated in a special apparatus to yield m-xylyl chloride without the production of dichloro-derivatives. The product was fractionally distilled and the composition of each fraction determined by its refractive index. The total yield of m-xylyl chloride, based on chlorine used, was 76%. The ratio between nuclear and side-chain chlorination was approximately 1:10. The presence of oxygen in the chlorine slowed down the chlorination tremendously and the product could not be distilled because of decomposition with evolution of hydrogen chloride. The following refractive indices were determined with an Abbé refractometer: m-xylene,  $n_D^{25} = 1.4955$ ; 4-chloro-1.3-dimethyl benzene,  $n_D^{25} = 1.5230$ ; m-xylyl chloride,  $n_D^{25} = 1.5327$ .

The side-chain chlorination of m-xylene presents a more difficult problem than arose in the case of toluene<sup>1</sup>. If chlorine be bubbled into boiling m-xylene, not only m-xylyl chloride is formed, but also 4-chloro-1.3-dimethyl benzene and dichloro-derivatives of m-xylene. Since the boiling point of m-xylyl chloride lies intermediate between that of the nuclear chlorinated product and that of the dichloro-derivatives, its isolation from such a mixture is difficult. Attempts were consequently made to prevent or materially reduce the production of all chlorinated products except m-xylyl chloride. We were successful in preventing the formation of dichloro-derivatives and, by so doing, simplified the fractional distillation and obtained good yields of product.

The xylene used in these experiments was purified by the method of Spannagel and Tschunker<sup>2</sup>. Technical m-xylene, B. Pt. 137-139°, was cooled in a bath of dry ice and alcohol to below -55°. There was a copious crystallization of p-xylene. The unfrozen m-xylene was sucked out by inverted filtration.

<sup>1</sup> King and Beazley, *Proc. N. S. Inst. Sci.* **18**, 204-212 (1934).

<sup>2</sup> Spannagel and Tschunker, *Ger. Pat.* 567,331, Dec. 16, 1927; *C. A.* **27**, 1366 (1933)

In the chlorinations we wished to know the exact amount of chlorine used. The large tanks of liquid chlorine could not be weighed with sufficient accuracy, so chlorine was transferred to a small cylinder weighing approximately 500 gms. The small cylinder, connected to the large one by a piece of sulphur-free rubber tubing well wired on, was cooled with dry ice in alcohol. The large tank was turned on and the pressure regulated by noting the swelling of the rubber tubing. In a very short time a sufficient weight of chlorine had been liquified in the small cylinder. To free the chlorine from any admixed oxygen, the valve to the small cylinder was opened before the cylinder had warmed up and a small amount of chlorine was allowed to escape.

After several trials the chlorinating apparatus illustrated in Fig. I was constructed. With this chlorinator the dichlorination of xylene was almost entirely prevented for a large excess of xylene vapor was rapidly mixed with a slow stream

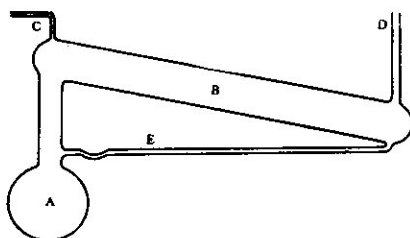


Fig. I.

of chlorine and the products were immediately removed to prevent further admixture with chlorine. The apparatus was of Pyrex glass throughout. A 500 cc. distilling flask (A) was used, though a larger one could be substituted without changing the dimensions of the rest of the apparatus. The neck of this flask ( $\frac{3}{4}$  inch in diameter and 5 inches long) was sealed into one end of the chlorinating chamber (B) which was 20 inches long and 2 inches in diameter. The chlorine inlet (C) was of  $\frac{1}{2}$  mm. capillary tubing set directly opposite to the centre of the neck of the distilling flask. The apparatus was sealed to an

efficient reflux condenser at (D) which in turn was connected to the hydrogen chloride absorbers. The reflux was returned to the distilling flask through (E). The chlorinating chamber was illuminated by a 500 watt, nitrogen-filled bulb. In a preliminary experiment, the chlorine inlet was of  $\frac{1}{4}$  inch tubing sealed in line with the chlorinating chamber instead of at the top. This was found unsatisfactory. A small amount of dichlorinated derivatives was produced. Unless the flow of chlorine was cut very low, part of it passed unreacted to the absorbers. There was a tendency for condensed liquid to back up the wide tube against the flow of chlorine.

The following description of a typical chlorination illustrates the method. 260 gms. of m-xylene were put into the distilling flask and boiled until all water had been swept out of the apparatus through the uncooled condenser into the absorbers. Then the condenser was cooled and the rate of boiling was regulated so that refluxing took place only in the lower end of the condenser. The light was turned on and 126 gms. of chlorine (determined by loss of weight of cylinder), dried by sulphuric acid, were passed in at the rate of about 40 gms. per hour. After the chlorination was complete, 17 gms. of xylene were found in the absorbers, so that 243 gms. of xylene were used in the chlorination. The product weighed 305 gms.

300 gms. of the product were analyzed by fractional distillation using the method previously described<sup>2</sup>. Table I and Fig. II give the results. The residue in this distillation, 18.7 gms., was much larger than in the case of the similar analysis of crude benzyl chloride<sup>1</sup>. It seemed to be tarry in character rather than composed of dichloro-xylene derivatives.

Since there was no distinct break in the distillation curve corresponding to 4-chloro-1,3-dimethyl benzene, some of this substance was prepared in a separate experiment by bubbling chlorine into m-xylene in the presence of iodine as a catalyst. The nuclear chlorinated product was fractionated and the pure fractions had a constant refractive index of  $n_D^{25} = 1.5230$ .

TABLE 1.  
*Analysis of Chlorinated m-Xylene.*

Fraction	Wt. gms.	$n_D^{25}$	Wt. m-xylene	Wt. chloro-xylene	Wt. m-xylene chloride
1	6.41	1.4950	6.41	.....	.....
2	36.10	1.4955	36.10	.....	.....
3	5.41	1.4955	5.41	.....	.....
4	5.91	1.4956	5.89	0.02	.....
5	4.62	1.4961	4.52	0.10	.....
6	2.22	1.4964	2.15	0.07	.....
7	1.21	1.4966	1.16	0.05	.....
8	1.38	1.4967	1.32	0.06	.....
9	2.17	1.4974	2.02	0.15	.....
10	1.90	1.4981	1.72	0.18	.....
11	1.84	1.5005	1.51	0.33	.....
12	2.54	1.5167	0.58	1.96	.....
13	2.33	1.5230	.....	2.33	.....
14	2.92	1.5252	.....	2.26	0.66
15	2.96	1.5270	.....	1.74	1.22
16	2.67	1.5282	.....	1.24	1.43
17	3.26	1.5293	.....	1.14	2.12
18	3.21	1.5300	.....	0.89	2.32
19	4.17	1.5302	.....	1.07	3.10
20	4.02	1.5304	.....	0.95	3.07
21	3.98	1.5306	.....	0.86	3.12
22	3.57	1.5308	.....	0.70	2.87
23	4.11	1.5312	.....	0.64	3.47
24	4.12	1.5313	.....	0.59	3.53
25	4.22	1.5315	.....	0.52	3.70
26	3.90	1.5316	.....	0.44	3.46
27	4.34	1.5318	.....	0.40	3.94
28	4.07	1.5318	.....	0.38	3.69
29	4.54	1.5319	.....	0.37	4.17
30	5.52	1.5321	.....	0.34	5.18
31	6.31	1.5323	.....	0.26	6.05
32	5.55	1.5325	.....	0.11	5.44
33	5.12	1.5326	.....	0.05	5.07
34	5.45	1.5327	.....	.....	5.45
35	7.77	1.5327	.....	.....	7.77
36	43.27	1.5327	.....	.....	43.27
37	38.91	1.5327	.....	.....	38.91
38	2.50	1.5327	.....	.....	2.50
39	7.61	1.5327	.....	.....	7.61
40	6.63	1.5327	.....	.....	6.63
41	6.45	1.5327	.....	.....	6.45
42	4.63	1.5327	.....	.....	4.63
..	.....	.....	68.79	20.20	190.83

based on the chlorine from the cylinder, is 76%. If the yield be taken to be the fractions 30-42 inclusive, then the percentage yield is 59%. This can be considerably increased by re-fractionating the intermediate fractions.

In certain experiments using earlier forms of the chlorination apparatus, the refractive indices of the last fractions were greater than that of m-xylyl chloride, indicating the presence of dichlorinated products. With the final form of the chlorination apparatus there was no indication of the formation of dichloro-xylene derivatives. The distillation merely slowed down at the end and, when the heat under the still was increased and the pressure was reduced, the product became colored. This indicates that dichloro-derivatives are formed from the mono-chloro-derivatives and not directly from m-xylene.

Several attempts were made without success to decrease the amount of nuclear chlorination. It was hoped that the presence of oxygen would slow down nuclear chlorination more than side-chain chlorination<sup>4</sup>. Duplications of the above described chlorination were made with the exception that oxygen and chlorine were both added in about equal volumes. The chlorination was very slow. Though it took 26 hours to add 132 gms. of chlorine, much went through unreacted to the absorbers. The product was very dark in color. On heating the product, hydrogen chloride was evolved at such a rate that fractionation was impossible. Possibly a Friedel and Crafts reaction took place, the oxidized products acting catalytically. Or it is possible that a large amount of an addition product between m-xylene and chlorine was present and, on heating, decomposed with the elimination of hydrogen chloride.

We wish to acknowledge our indebtedness to Mr. C. C. Forward, Dominion Government Analyst, who loaned us the Abbé refractometer used in this investigation.

<sup>4</sup> Hannon and Kenner, *J. Chem. Soc.* 1934, 138.