

## SIDE-CHAIN CHLORINATION OF AROMATIC COMPOUNDS IN THE VAPOUR PHASE

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According to the literature, the ethoxy- and methoxy-benzyl chlorides are prepared by the action of phosphorus trichloride or thionyl chloride on the corresponding alcohols. Ethyl and methyl ethers of *ortho*-, *meta*- and *para*-cresols on chlorination in the vapour phase have yielded these chlorides, the yield in the case of the *ortho*-compound being 60-65%, the *meta* and *para* compounds furnishing 25% and 30% respectively. *Ortho*-, *meta*- and *para*-xylenes yield 50-80% of the corresponding xylyl chlorides. The chloro derivatives of anisole and cineol were obtained for the first time by the vapour phase chlorinations. Sunlight favours these side-chain chlorinations. The vapour phase chlorination of *ortho*-, *meta*- and *para*-nitrotoluenes was not successful, although these chlorinations are known to proceed well in the liquid phase.

In the chlorination of toluene, substitution may take place either in the nucleus or in the methyl group. Nuclear substitution takes place when the halogen acts on toluene in presence of iodine or other halogen carriers. Side-chain substitution occurs when the halogen acts on boiling toluene or in presence of direct sunlight, the influence of light being greater than that of heat in inducing substitution in the side-chain (Cohen, Dawson, Blockley and Woodmansey, *J. Chem. Soc.*, 1910, 97, 1623; Bancroft, *J. Phys. Chem.*, 1908, 12, 240, 417). The side-chain chlorinated derivatives of aromatic hydrocarbons, particularly those of toluene, are of great technical importance.

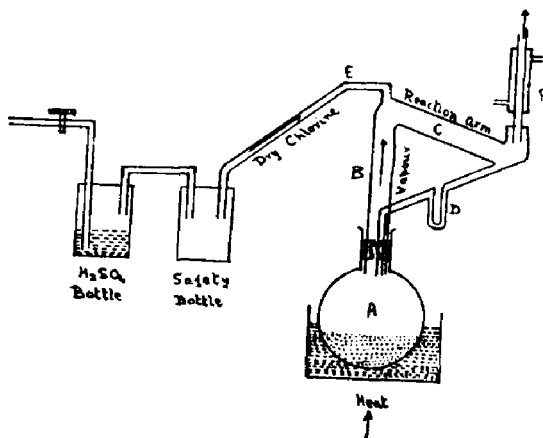
Vapour phase chlorination of toluene has been studied by Mason *et al* (*J. Chem. Soc.*, 1931, 3150) in which chlorine reacts smoothly with an excess of toluene vapours at temperatures above 250° in the absence of specific chlorine carriers, the products being chiefly benzyl and benzal chlorides. The preparation of the side-chain halogen substitution products of toluene has been effected by Gibbs and Geiger (*U. S. patent*, 12,46,739, 1917) in the vapour phase, in the presence of ultraviolet light. Generally substitution in the side-chain is favoured at higher temperature; whilst in the presence of a catalyst or a halogen carrier, the replacement of nuclear hydrogen takes place at a lower temperature.

A survey of the literature revealed that the vapour phase chlorination of the methyl cresyl ethers has not been done. The principle of the vapour phase chlorination of toluene as indicated above has now been extended for the methyl and ethyl cresyl ethers, xylois, nitrotoluenes and some other aromatic compounds, to get the corresponding side-chain substituted halides. In the present investigation, these side-chain substituted chlorides have been obtained by chlorinating cresyl ethers in the vapour phase instead of the usual method of obtaining them in the liquid phase by the use of phosphorus oxychloride or thionyl chloride on the corresponding alcohols (Pschorr, *Ber.*, 1900, 33, 165; *Annalen*, 1912, 391, 44; Königs and Bernhart, *Ber.*, 1908, 41, 499; Pschorr and Zeidler, *Annalen*, 1910, 373, 76; Rayman, *Bull., soc. chim.*, 1876, ii, 26, 534, 43; Radziewanowski and Schram, *Chem. Zentr.*, 1898, I, 1019).

In this investigation no catalyst or halogen carrier has been used. The chlorination apparatus is kept in sunlight which favours the side-chain chlorination. A special, but a very simple apparatus, has been described for the vapour phase chlorination.

## E X P E R I M E N T A L

*Chlorination Apparatus.*—Chlorination was carried out in a specially designed pyrex glass apparatus as shown in the diagram. The flask A was joined to the arm B of the triangle with a ground glass joint. Chlorine from the chlorine cylinder was dried by passing through concentrated sulphuric acid and was admitted at E. The rate of passing of the chlorine could be easily regulated. An empty safety bottle was used as a precaution against back suction. There was inserted a U-tube in the narrow tube D for preventing the vapours from travelling up and disturbing the regular flow of the condensed liquid back to the flask A.



*Chlorination of the substance.*—The substance to be chlorinated was kept in the flask A which was heated in an oil-bath or metal-bath depending upon the boiling point of the substance to be chlorinated. The vapours of the substance came in contact and reacted with the dry chlorine vapours in the side arm C. This portion was as far as possible kept exposed to direct sunlight.

The chlorinated substance was condensed back by the double surface condenser F back to the flask A through a narrow tube D as shown. The end-point in the process of chlorination was known (i) when no vapours were generated, the chlorinated substance possessing invariably a much higher boiling point than that of the original substance, and (ii) by knowing the increase in weight of the substance due to chlorination.

*Isolation and Identification of the Products.*—The product after getting rid of excess of chlorine by repeatedly shaking with water, dilute alkali and again with water, was fractionally distilled under reduced pressure, the various fractions collected and identified in all cases by their boiling points and in most cases also by a study of the products of hydrolysis.

*A typical experiment on Chlorination and Identification of the Products.*—The *o*-cresol methyl ether (75 g.), b.p. 177°, prepared according to the method of Pinette, (*Ber.*, 1903, 36, 1804; *Annalen*, 1888, 243, 32, 37), was taken in the flask of the chlorination apparatus. The temperature of the oil-bath was kept at 180°. Chlorine was passed and the vapour

TABLE I

*Chlorination of cresol ethers*

No.	Compound.	B.p.	Quantity taken for chlorination.	Temp. of the bath.	Time taken.	Products after chlorination.	References.
1.	<i>o</i> -Cresol methyl ether	171°	100 g.	190-95°	2½ hrs.	60-65% yield of 2-methoxybenzyl chloride, b.p. 111-112°/11 mm. Chlorination mostly in the side-chain	Pechorr, <i>Ber.</i> , 1900, 33, 165. Chlorination in the liquid phase gives b.p. 111-112°/11 mm.
2.	<i>m</i> -Cresol methyl ether	177°	100	Do	2½	25% of <i>m</i> -methoxybenzyl chloride, b.p. 124°/13 mm. 40% nuclear substituted products, b.p. 95-100°/13 mm. (b.p. 185°)	Pechorr ( <i>Annalen</i> , 1912, 391, 44). PCl <sub>3</sub> on 3-methoxybenzyl alcohol gives the chloride, b.p. 124°/13 mm.
3.	<i>p</i> -Cresol methyl ether	175°	100	100-200°	2½	25% of 4-methoxybenzyl chloride, b.p. 115-116°/15 mm. 40% nuclear substituted products, b.p. 100-105°/15 mm. 20% unconverted; 5% tar	Königs, Bernhart. ( <i>Ber.</i> , 1908, 41, 499). Chlorination in the liquid phase; 4-methoxybenzyl chloride, b.p. 115°-116°/15 mm.
4.	<i>o</i> -Cresol ethyl ether	190°	90	220-30°	4	Chief product: 75% of <i>o</i> -ethoxybenzyl chloride, b.p. 216-220°; b.p. 125°/15 mm.	Chlorinating the corresponding alcohol (Pechorr and Zeidler, <i>Annalen</i> , 1910 373, 76);, b. p. 125°/15 mm.
5.	<i>m</i> -Cresol ethyl ether	192°	80	220-40°	4	About 30% of <i>m</i> -ethoxybenzyl chloride b.p. 250°, and mostly in the nucleus	
6.	<i>p</i> -Cresol ethyl ether	189°	120	Do	4½	Chlorination gives many complex substituted products. One fraction below 210° and the other above 200°	Products unidentified
7.	Anisole	155°	100	180°	2½	80% <i>o</i> -chloroanisole, 195°-96° some <i>p</i> -chloroanisole, b.p. 88°/18 mm.	Henry ( <i>Ber.</i> , 1869, 2, 710) Fische ( <i>Ber.</i> , 1878, 11, 1463) (Liquid phase chlorination)

TABLE II

*Chlorination of other compounds*

No.	Compound.	B.p.	Quantity taken for chlorination.	Temp. of the bath.	Time taken in hr.	Products after chlorination.	References for the preparation of the same products in the liquid phase.
1.	Toluene	111°	200 g.	150-170°	4	80-85% conversion to benzyl chloride, b.p. 179°	Recovered toluene could again be used
2.	<i>o</i> -Xylene	140°	75	190-200°	3	50-55% conversion to <i>o</i> -xylene chloride, b.p. 197-200°	Chlorination in 2, 3 and 4 is accompanied by tar formation giving low yields, in the vapour phase. Reaction proceeds almost entirely in the side-chain and is facilitated by sunlight
3.	<i>m</i> -Xylene	138°	75	Do.	3	55-60% conversion to <i>m</i> -xylene chloride, b.p. 195-97° 10% xylyl dichloride, b.p. 250°	
4.	<i>p</i> -Xylene	136°	75	Do.	3	60% conversion to <i>p</i> -xylyl chloride, b.p. 200-202° and 10% dichloride, b.p. about 254°	These chloro compounds fume very strongly in air. These side chain chlorinated products compare well with those obtained by Rayman ( <i>Bull. soc. chim.</i> , 1874 <i>vi</i> , 26, 534, 43)
5.	<i>o</i> -Nitrotoluene	220°	100	220-230°	9	No chlorination probably due to the steric hindrance of the nitro group	Radziewanowski and Schram, <i>Chem. Zentr.</i> , 1898, I, 1019
6.	<i>m</i> -Nitrotoluene	232°	80	230-240°	6	No chlorination in the vapour phase	The chlorination in the liquid phase (for 6 and 7) goes smoothly
7.	<i>p</i> -Nitrotoluene	237°	40	240-250°	6	No chlorination in the vapour phase	Hansermann and Beck, <i>Ber.</i> , 1892, 25, 2445
8.	Cineol $C_{15}H_{18}O$	176°	80	190-200°	4	Chlorocineol, b.p. 230-35°	<i>Ber.</i> , 1884, 17, 1978. Carl Hell and Ritter obtained the same, b.p. about 230°

of the *o*-cresol methyl ether reacted with the chlorine (preferably in sunlight) in the arms of the triangle. Chlorine was passed till completion of the reaction as indicated by (i) and (ii) mentioned above.

The product, thus obtained, after being freed from free chlorine was fractionally distilled under reduced pressure. The fraction distilling between 110° and 115°/11 mm. was collected and again fractionally distilled. The fraction boiling at 111-112°/11 mm. was collected; yield 62.4 g. (nearly 65%).

*Hydrolysis.*—The fraction boiling at 111-112°/11 mm. (5 g.) is *o*-methoxybenzyl chloride. This was heated with alcoholic potash solution (2 *N*) for about 20 hours, and the reaction product after being worked up in the usual manner furnished pure *o*-methoxybenzyl alcohol (4 g.), b. p. 250°. Pschorr (*Ber.*, 1900, 33, 165) gets the *o*-methoxybenzyl alcohol (b.p. 248°-50°). This confirms that the original fraction was *o*-methoxybenzyl chloride.

The chlorination of the *ortho*- and *para*-methyl cresyl ethers, as also of *ortho*-, *meta*- and *p*-ethers of cresols and of *ortho*-, *meta*- and *para*-xylenes was carried out exactly as above. The vapour phase chlorination of the nitrotoluenes was not successful. Cineol and anisole were chlorinated for the first time in the vapour phase.

The results of the chlorination of the different compounds carried out in the vapour phase are given in Table I, II and III.

TABLE III

*Estimation of chlorine and hydrolysis*

No.	Compound.	% of chlorine		Hydrolysis product.	References for the preparation of the same products.
		Calc.	Found.		
1.	<i>o</i> -Methoxybenzyl chloride	22.66	23.00	<i>o</i> -Methoxybenzyl alcohol, b.p. 254-55°	Pschorr <i>et al</i> ( <i>Ber.</i> , 1900, 33, 165) obtained the alcohol b.p. 250°
2.	<i>m</i> -Methoxybenzyl chloride	Do.	22.8	<i>m</i> -Methoxybenzyl alcohol, b.p. 250°	<i>cf.</i> Mettler, <i>Ber.</i> , 1906, 39, 2939; b.p. of <i>m</i> -methoxy alcohol 250°
3.	<i>p</i> -Methoxybenzyl chloride	Do.	22.63	Anisyl alcohol, b.p. 255-58°	<i>Annalen</i> , 1856, 98, 169, b.p. 255-58°
4.	<i>o</i> -Ethoxybenzyl chloride	20.82	20.8	<i>o</i> -Ethoxybenzyl alcohol, b.p. 254°	Alcohol obtained by Botsch ( <i>Montash</i> , 1880, 1, 621) b.p. 254°
5.	<i>m</i> -Ethoxybenzyl chloride	Do.	21.02	..	..
6.	<i>p</i> -Ethoxybenzyl chloride	Do.	20.96	..	..
7.	<i>o</i> -, <i>m</i> - and <i>p</i> -Xylyl chlorides	25.2	25.06 25.21 25.60	..	Gundelach, <i>Bull. soc. chim.</i> , 1876, 26, 43 Reyman, <i>Bull. Soc. chim.</i> , 1876, 26, 534

The boiling points have been corrected as to be under normal pressure.

## DISCUSSION

The main products formed in this process of chlorination, *e.g.* with toluene, xylenes and the *ortho*-ethers of the cresols, are side-chain substitution products. The compounds containing chlorine in the ring are also formed, sometimes more than one, rendering the separation of these products rather difficult. But when the reaction is carried out in the sunlight and the operation properly controlled, chlorination proceeds mostly in the side-chain.

The following points require specific mention in connection with the experiments conducted in the vapour phase chlorinations :

(i) If there is not an excess of the vapours of the substance to be chlorinated, there is a fire in the apparatus ; therefore, chlorine is regulated from time to time so that it is never in excess of the vapour of the substance.

(ii) In these chlorinations there is always a tarry product formed due to the high temperature of the heating bath ; hence it is essential to avoid unnecessary high temperatures as far as possible. Because of the tar formation at the high temperature, yields are very low in some cases.

The chlorination of toluene yields very good results (about 85% conversion) yielding benzyl chloride. This is a better way of chlorinating toluene than the usual laboratory method of chlorinating in the liquid phase.

Throughout these chlorinations no halogen carrier or catalyst was used. Sunlight was found to be extremely useful for the side-chain chlorinations, improving the yields in the case of *ortho*-, *meta*- and *para*-methoxy and ethoxy-benzyl chlorides.

The chlorination of the nitrotoluenes was expected to proceed in the side-chain specially in the case of the *meta* and *para* compounds. The *ortho* compound may not be chlorinated because of the steric hindrance of the nitro group in the compound. The side-chain chlorination of the *meta* and *para* compounds has, however, been carried out in the liquid phase (Hanssermann and Beck, *Ber.*, 1892, 25, 2445). The results are negative in the vapour phase even after prolonged chlorination.

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