

Chlorination of Arylammonium Salts in Sulphuric Acid

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Aromatic amines (aniline, *o*-toluidine, and *p*-toluidine) were dissolved in concentrated sulphuric acid and chlorinated with chlorine gas. At room temperature, chlorination was very selective, occurring *ortho* or *para* to the methyl group. In the absence of an activating methyl group, chlorination was slow. Dichlorination did not occur. For comparison, the amine–aluminium chloride–hydrogen chloride complexes were chlorinated.

PREPARATION of *ortho*- and *para*-chlorinated aromatic amines is usually accomplished by chlorinating an amine in dilute acid solution or by chlorinating an *N*-acyl derivative. A *meta*-chloro-amine is usually prepared in two steps: halogenation of the nitroaromatic precursor and reduction of the halogenated nitro-compound. In an attempt to prepare *m*-chlorinated amines directly from amines, ammonium salts dissolved in concentrated sulphuric acid have been chlorinated.

Chlorinations of aniline, 2-methylaniline, and 4-methylaniline in the temperature range 25–50 °C led to simple product mixtures with no dichlorination. Chlorine entered *ortho* or *para* to the methyl group.

2-Methylaniline was studied in detail. Product compositions are summarised in the Table. The orient-

TABLE 1

Dependence of products upon temperature in the chlorination of 2-methylanilinium ion in 95.9% sulphuric acid

Temperature (°C)	Relative rate	Products (%)			
		3-Cl	4-Cl	5-Cl	6-Cl
25		51	0	49	0
35	0.4	54	0	46	0
50	1.0	57	<0.5	43	<0.5

ation in the substitution may be compared with the selectivity in chlorinating the 2-methylaniline–aluminium chloride–hydrogen chloride complex at 80 °C (3-chloro, 51%; 4-chloro, 7%; 5-chloro, 39%; 6-chloro, 3%). A comparison may also be made with iron halide-catalysed chlorination of 2-nitrotoluene: reaction with chlorine in the presence of iron and iodine at 50–60 °C gives 6- and 4-chloro-2-nitrotoluene in the ratio 2 : 1.¹ These results suggest that the chlorinating reagent in sulphuric acid has higher selectivity for the position *para* to methyl than the chlorinating reagents in the other two systems. Moreover, the almost exclusive *ortho*- or *para*-orientation of chlorine in the products is consistent with attack by mildly electrophilic diatomic halogen, rather than a more highly reactive, less discriminating species.

Chlorination of the 4-methylanilinium ion in sulphuric acid gave only 3-chloro-4-methylaniline. As in the case of 2-methylaniline, monochlorination was permitted at

the moderate temperature but the combined influence of two deactivating substituents (Cl and NH₃⁺) and only one activating (CH₃) made the substrate insufficiently nucleophilic for dichlorination.

Reactions with anilinium ion in sulphuric acid revealed that one deactivating group (NH₃⁺) with no activating group was sufficient almost to stop chlorination at the moderate temperatures of this study. The chlorinating reagent is less reactive than the nitrating reagent in nitric acid–sulphuric acid, which gave nitroanilinium ions under similar conditions.²

For comparison, amine–aluminium chloride–hydrogen chloride complexes were chlorinated according to Pearson's procedure.³ Pearson and his co-workers had reported chlorination of aniline to give the three monochloroanilines and 2,5- and 3,4-dichloroanilines, and chlorination of 4-methylaniline to give 3-chloro-4-methylaniline. They speculated that the coloured amine–aluminium chloride–hydrogen chloride complexes were tetrachloroaluminate(III) salts of cations with the extra hydrogen atom attached to the amine by a σ bond to nitrogen or to carbon. Our results differed slightly from Pearson's observations. More important results, however, were that product mixtures from reactions of the arylammonium ions with chlorine in sulphuric acid were more simple than those from chlorinating the amine–aluminium chloride–hydrogen chloride complexes.

G.l.c. was used for qualitative and quantitative analyses. The silicone SE-30 stationary phase was used for analysing all chloroaniline and dichloroaniline products except 3- and 4-chloroaniline. These isomers were analysed with Siponate DS-10 stationary phase,⁴ which selectively retards *para*-disubstituted isomers. The latter column was also used to analyse products from chlorinations of the methylanilines.

In 1889 Hafner⁵ reported the following chlorinations in concentrated sulphuric acid: aniline to 4-chloroaniline; 4-methylaniline to 3- and 2-chloro-4-methylaniline; and 2-methylaniline to an unidentified product. Low yields of isolated amines or solid derivatives were obtained. Hafner's errors and the unavailability of suitable analytical methods have hitherto prevented the synthetic usefulness of chlorinations in sulphuric acid from being recognized.

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EXPERIMENTAL

Materials.—Concentrated sulphuric acid was the commercial grade with 4.1% water, as determined by Karl Fischer titration. All amines were the highest quality commercial materials and were redistilled or recrystallized before use.

Analyses.—G.l.c. was used for qualitative and quantitative analyses. Detection was performed by thermal conductivity measurement. For an 8 ft \times 1/8 in column packed with 10% SE-30 (methyl silicone polymer) on Chromosorb W operating isothermally at 150 °C with a helium flow rate of 60 ml min⁻¹, the following retention times (min) were observed: aniline, 0.6; 2-chloro, 1.0; 3-chloro, 1.26; 4-chloro, 1.32; 2,6-dichloro, 1.5; 2,4-dichloro, 2.04; 2,5-dichloro, 2.2; 2,3-dichloro, 2.6; 3,5-dichloro, 2.9; 3,4-dichloro, 3.4; 2,4,5-trichloro, 5.4; 3,4,5-trichloro, 6.3; 2-methyl, 0.83; 3-chloro-2-methyl, 1.9; 5-chloro-2-methyl, 1.9; 6-chloro-2-methyl, 1.9; 4-chloro-2-methyl, 1.95; 4-methyl, 0.86; 3-chloro-4-methyl, 1.9. For a 6 ft \times 1/8 in column packed with 15% Siponate DS-10 (sodium dodecylbenzenesulphonate) on sodium hydroxide-treated Chromosorb⁴ operating isothermally at 180 °C with a helium flow rate of 60 ml min⁻¹, the following retention times (min) were observed: aniline, 1.1; 2-chloro, 1.8; 3-chloro, 4.0; 4-chloro, 5.0; 2-methyl, 1.4; 6-chloro-2-methyl, 2.0; 5-chloro-2-methyl, 4.8; 3-chloro-2-methyl, 5.2; 4-chloro-2-methyl, 6.5; 4-methyl, 1.5; 2-chloro-4-methyl, 2.5; 3-chloro-4-methyl, 5.2.

Chlorinations in Sulphuric Acid.—(a) *2-Methylanilinium ion.* A 1-l flask was equipped with thermometer, outlet to a scrubber, pressure-equalising dropping funnel, stirrer, and gas addition tube for nitrogen. All apparatus had been oven-dried and flushed with dry nitrogen during and after assembly.

Concentrated sulphuric acid (800 g, ca. 8 mol) was added, the stirrer was started, and temperature was reduced below 0 °C (solid CO₂-acetone bath). This temperature was maintained while 2-methylaniline (214.4 g, 2.0 mol) was added dropwise (30 min). A heating mantle controlled by a Thermowatch was substituted for the cooling bath and the slurry was warmed. Heating time from 0 to 50 °C was 25 min. Before the temperature had reached 50 °C, the salt had dissolved. During this time, chlorine was collected in a cold trap (solid CO₂). A gas addition tube was attached to the cold trap. Then the chlorine gas delivery tube was attached to the flask in place of the nitrogen delivery tube. When the temperature reached 50 °C, introduction of chlorine was started at the greatest rate that would not make the scrubber water yellow. The delivery rate was controlled by gradually lowering the flask containing solid CO₂ from around the trap. After 10 h, chlorine passage was stopped. The mixture was quickly added to wet ice (2 kg) with stirring. The mixture was cooled in an ice-water bath and kept below 25 °C while aqueous 33% sodium hydroxide was added (to pH 11). The mixture was extracted with ether. The extracts were combined, dried (MgSO₄), and filtered. Under nitrogen, most of the ether was evaporated off. The solution was distilled without fractionation and 260 g of material was collected over the range 90–106 °C at 10 mmHg. This distillate contained 2-methylaniline (0.18 mol, 9% recovery), 3-chloro-2-methylaniline (0.97 mol, 48.5%), 5-chloro-2-methylaniline (0.73 mol, 36.5%), and <0.5% of 4- and 6-chloro-2-methylaniline.

(b) *4-Methylanilinium ion.* As described for 2-methylaniline, 4-methylaniline (1 mol) was dissolved in concentrated

sulphuric acid (6 mol) and treated with chlorine at 25 °C for 6 h. The products were 3-chloro-4-methylaniline (77%) and unchanged 4-methylaniline (23%).

(c) *Anilinium ion.* As described for 2-methylaniline, aniline (1 mol) was dissolved in concentrated sulphuric acid (6 mol) and treated with chlorine at 25 °C for 4 h. The product was essentially all aniline, with traces of monochloroanilines. The reaction was repeated at 70 °C for 6 h. The products were 2-chloroaniline (2%), 3-chloroaniline (3%), 4-chloroaniline (3%), and unchanged aniline (92%).

Chlorination of Amine-Aluminium Chloride-Hydrogen Chloride Complex.—(a) *Aniline.* A 500 ml flask was equipped with thermometer, outlet tube to a scrubber, dropping funnel, mechanical stirrer, and ice-water bath. All apparatus had been oven-dried and flushed with nitrogen during and after assembly. Aluminium chloride (222 g) was added. Then aniline (74.5 g, 0.8 mol) was added dropwise. During aniline addition, the temperature of the thick paste rose to 100 °C. The funnel was replaced by a tube to introduce hydrogen chloride beneath the surface of the complex, and the cooling bath was removed. As hydrogen chloride was added, the stiff paste changed to a dark, transparent liquid and the temperature rose to 105 °C. After 28 g of hydrogen chloride had been absorbed (1 h), the temperature fell. Chlorine (25.5 g, 0.36 mol) was condensed in a cold trap. The cold trap was fitted with a gas delivery tube. The hydrogen chloride delivery tube was replaced with the chlorine delivery tube. A heating mantle was used to keep the reaction mixture in the temperature range 80–85 °C, slightly above the temperature of the transition from semisolid complex to fluid complex. Chlorine was introduced below the surface of the fluid complex at a rate such as to keep the scrubber water from becoming yellow. After 3 h, all the chlorine had been absorbed. The hot mixture was poured over ice (750 g) with stirring. The suspension was cooled and made alkaline with aqueous 25% sodium hydroxide. The solution was extracted with ether, the extracts were combined and dried (MgSO₄), and the suspension was filtered and analysed. Present were 2-chloroaniline (7%), 3-chloroaniline (21%), 4-chloroaniline (10%), a trace of 2,5-dichloroaniline, and aniline (62%).

Other chlorinations of the aniline-aluminium chloride-hydrogen chloride complex were continued until as much as 2.2 mol of chlorine had been absorbed per mol of aniline. Product compositions are summarised in Table 2. Not

TABLE 2

Proportions (%) of amines in product from chlorination of aniline-aluminium chloride-hydrogen chloride complex at 80 °C.

Amine	Molar ratio of aniline to chlorine			
	1 : 0.7	1 : 1.0	1 : 1.2	1 : 2.2
Aniline	39	18	11	None
2-Chloro	10	11	12	1
3-Chloro	34	42	42	1
4-Chloro	16	21	23	3
2,3-Dichloro	None	1	2	11
2,4-Dichloro	None	None	None	Trace
2,5-Dichloro	1	3	4	33
2,6-Dichloro	None	None	None	None
3,4-Dichloro	None	4	5	43
3,5-Dichloro	None	None	None	Trace

shown in Table 2, but present after 2.2 mol of chlorine had been absorbed, was a mixture of trichloroanilines (8%), which were not separated and identified.

(b) *2-Methylaniline*. As described for the aniline complex, the 2-methylaniline complex at 80 °C was treated with chlorine until 1 mol of chlorine had been absorbed. The products were 3-chloro-2-methylaniline (39%), 4-chloro-2-methylaniline (5%), 5-chloro-2-methylaniline (30%), 6-chloro-2-methylaniline (2%), and unchanged 2-methylaniline (19%).

(c) *4-Methylaniline*. As described for the aniline complex, the 4-methylaniline complex at 80 °C was treated with chlorine until 1 mol of chlorine had been absorbed. The products were 3-chloro-4-methylaniline (89%), a trace of 2-chloro-4-methylaniline, and unchanged 4-methylaniline (11%).

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