Aromatic Nuclear Chlorination by Copper(II) Chloride 1

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Reactive phenols are chlorinated by copper(II) chloride in a toluene suspension, and in aqueous solution. In water the reaction is markedly accelerated by aluminium, chromium, and vanadyl chlorides, and by hydrogen chloride. Concentrated hydrochloric acid is the preferred medium for the reaction; in the presence of oxygen, copper(II) chloride is regenerated continuously. The p-chloro-derivatives of phenol, m-xylenol, and o-cresol are obtained in 90% yield.

Aromatic amines are similarly chlorinated preferentially at the para-position by copper(II) chloride, but reaction with anthracene gives anthraquinone.

COPPER(II) chloride has been used for the chlorination of a variety of active hydrogen compounds.² Two types of reaction may be distinguished. In non-polar solvents, copper(II) chloride is not dissolved and chlorination occurs as a heterogeneous reaction on the surface; the rate is unaffected by the copper(I) chloride produced. With hydroxylic solvents a second mechanism operates; chlorination occurs in solution and the reaction is severely retarded by the copper(I) chloride produced.

Some substrates (e.g. anthracene) are chlorinated readily only under heterogeneous conditions.³ On the other hand, polar substrates such as aliphatic aldehydes and ketones react rapidly only under homogeneous conditions.²

The chlorination of phenols is important industrially and for most purposes the *para*-chlorinated isomers are were chlorinated by a common mechanism involving the simultaneous one-electron reduction of two copper(II) species.

To improve the conversion of 3,5-xylenol into the germicide 4-chloro-3,5-xylenol, the heterogeneous conditions used by Nonhebel³ were tried. With toluene as diluent, the use of a slight excess of copper(II) chloride gave a rapid reaction at ca. 90° and 4-chloro-3,5-xylenol was isolated in 93% yield. However, the reaction rate was markedly dependent upon the purity of the reactants, and at higher temperatures the specificity of the chlorination was reduced.

Extension of this method to other phenols showed that 3,5-xylenol had given a particularly favourable result. Phenol itself gave a slower reaction and much polymer. p-Cresol gave 3-chloro-4-hydroxytoluene in only 25%

TABLE]	L
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Effect of solvent on chlorination of phenol by copper(II) chloride

products (mole %)	Yield of prod								
$rac{p-Cl}{2,4-Cl_2}$ $rac{rac{rac}{w/w}}{(w/w)}$	henol o-Cl	, j	Solvent Conditions	Solvent					
6.8 13.6 0.5 43	34.7 3.8	,	e 14 h, 104°	Foluene					
No reaction	No re		icetate 1 h. 85°	Ethvl acetate					
-5 39.5 2.5 20	$22 \cdot 4$ 12.5	•	acetate $7 h, 132^{\circ}$	Pentyl acetate					
3.0 26.1 0.1 28	24.7 8.0	•	ne $7 h. 115^{\circ}$	n-Decane					
··5 81·2 17	7.5)	11 h, 100°	Phenol					
5.7 46.8 4.2 22	28.4 5.7	`	acid 11 h, 117°	Acetic acid					
$6 \cdot 4 55 \cdot 3 1 \cdot 1 6$	40·3 5·4	,	* 7 h, 108°	Water *					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{ccccccc} & & & & & & & & \\ 22\cdot4 & & & & & & & \\ 24\cdot7 & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ 28\cdot4 & & & & & & & \\ & & & & & & & & \\ 40\cdot3 & & & & & & & \\ \end{array}$, , ,	acetate 1 h, 35 acetate 7 h, 132° ne 7 h, 115° 11 h, 100° acid 11 h, 117° * 7 h, 108°	Pentyl acetate Pentyl acetate 1-Decane Phenol Acetic acid Water *					

* See Experimental section

required. Many attempts ⁴ have been made to increase the *para-ortho* ratio of 1.7:1 found with molecular chlorine as chlorinating agent.⁵ The chlorination of phenol by copper(II) chloride,⁶ under anhydrous conditions with an excess of phenol as diluent, gave a p- to o-chlorophenol ratio of 10:1. However, with water as solvent at 275° equal amounts of *o*- and *p*-chlorophenol were produced. It was concluded that 'the ratio of ortho- to para-halogenation increases when water is present, proportional to the amount of water.'

Kosower and his co-workers 7 showed later that phenol was rapidly chlorinated by copper(II) chloride in dimethylformamide solution, giving p-chlorophenol as the main product. They proposed that ketones and phenols

¹ For a preliminary account of part of this work see H. P. Crocker and R. Walser, *Chem. and Ind.*, 1969, 1141.

² A. Lorenzini and C. Walling, J. Org. Chem., 1967, **32**, 4008, and references therein.

³ D. C. Nonhebel, J. Chem. Soc., 1963, 1216; D. Mosnaim and D. C. Nonhebel, *Tetrahedron*, 1969, **25**, 1591.

yield; the major product was a viscous tar and small amounts of coupled products were also formed.

In view of these results, phenol was taken as substrate and a range of solvents was examined as shown in Table 1.

Phenol was chlorinated at a similar initial rate under both homogeneous and heterogeneous conditions. Surprisingly, in view of the earlier statement,⁶ the use of water gave a favourable *para-ortho* ratio and the lowest amount of polymer. However, in water the reaction was severely retarded by copper(I) chloride, and large excesses of copper(II) chloride were required to achieve a high conversion of phenol. The extent of polymeris-

⁴ B.P. 1,097,805, Sumitomo Chemical Company Ltd.; J. E. Kruger, Canad. P. 784,781 (Dow Chemical Co.)

⁵ G. H. Bing, W. W. Kennard, and D. N. Matthews, Austral. *J. Chem.*, 1960, 13, 317.
⁶ W. W. Kaeding and R. O. Lindblom, U.S.P. 2,805,263 (Dow Chemical Co.) (*Chem. Abs.*, 1958, 52, 2070).
⁷ E. M. Kosower, W. J. Cole, G.-S. Wu, D. E. Cardy, and C. Maistran, Lorg Chem. 1969, 29, 693

G. Meisters, J. Org. Chem., 1963, 28, 630.

ation was greatly increased in the presence of oxygen, and it was not practicable to remove copper(I) chloride by a simultaneous oxidation step. Since the system copper(I) chloride-amine-oxygen is widely used to convert phenols into high molecular-weight polyphenylene ethers,8 the occurrence of oxygen-catalysed polymerisation was not unexpected.

The addition of lithium chloride has been shown previously to enhance the rate of chlorination of aldehydes² and ketones,⁷ and to prevent the precipitation of copper (I) chloride. The qualitative effect of lithium chloride and a range of other halides on the chlorination of phenol was therefore examined.

The results in Table 2 show that the addition of any halide improved the rate, but the extent of improvement with salts of aluminium, beryllium, and chromium has been suggested previously,⁹ and there is spectroscopic evidence for the formation of a stable complex Cu- $(ZnCl_4)$.¹⁰

In subsequent experiments (Table 3) the effect of replacing the foreign metal salt with hydrochloric acid was examined. The effects of increasing the hydrochloric acid content of the reaction medium were entirely beneficial; the rate was increased, the polymer formation eliminated, and the para-ortho ratio was improved. Although Kochi¹¹ found the chlorination of acetone by copper(II) chloride to be retarded by hydrochloric acid, Lorenzini and Walling² contested this result, since the similar chlorination of isobutyraldehyde was markedly accelerated by hydrochloric acid.

Table	2
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Effect of metal salts on chlorination of phenol by copper(II) chloride	
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Additive	Nil	NaF	LiCl	MgCl ₂	CaC1 ₂	$ZnCl_2$	CdCl ₂	AlCl ₃	LaCl ₃	CeCl ₃	ZrOCl ₂	SnCl₄	VOC12	CrCl ₃	MnCl ₂	FeCl ₃	CoCl ₂	NiCl ₂
Product wt. (g)	1.9	1.5	$2 \cdot 3$	2.5	2.5	$2 \cdot 1$	$2 \cdot 1$	2.7	$2 \cdot 3$	$2 \cdot 4$	$2 \cdot 1$	$2 \cdot 3$	$2 \cdot 3$	2.8	$2 \cdot 5$	$2 \cdot 0$	$2 \cdot 4$	$2 \cdot 4$
Analysis (%) o-Cl Phenol 2,4-Cl ₂ <i>p</i> -Cl Polymer (mg)	2.8 69.9 Trace 27.5 78	9.4 58.6 1.3 30.7 927	$6.5 \\ 42.0 \\ 2.1 \\ 49.5 \\ 5$	$6.8 \\ 27.3 \\ 3.0 \\ 62.9 \\ 1$	$6.7 \\ 25.2 \\ 5.6 \\ 62.4 \\ 1$	$8.0 \\ 37.4 \\ 3.5 \\ 51.1 \\ 262$	$3.6 \\ 64.3 \\ 0.8 \\ 31.2 \\ 58$	$6.1 \\ 2.5 \\ 18.1 \\ 73.3 \\ 85$	$9.9 \\ 28.6 \\ 3.3 \\ 58.3 \\ 118$	$9.2 \\ 33.4 \\ 2.0 \\ 55.3 \\ 8$	$3.9 \\ 66.6 \\ 0.4 \\ 29.0 \\ 1$	8·9 8·0 16·7 66·5 276	$10.5 \\ 21.2 \\ 1.1 \\ 67.2 \\ 1$	7·1 2·7 9·9 80·3 18	$8.1 \\ 47.8 \\ 2.7 \\ 41.5 \\ 18$	$9.4 \\ 5.0 \\ 17.4 \\ 68.1 \\ 600$	$6 \cdot 1 \\ 33 \cdot 1 \\ 3 \cdot 2 \\ 57 \cdot 6 \\ 1$	$6 \cdot 4 \\ 32 \cdot 7 \\ 3 \cdot 4 \\ 57 \cdot 4 \\ 11$

was variable. In some cases, e.g. that of cadmium chloride, the effect was slight and acceleration by chloride ion 2 is clearly not the sole effect operating. In other cases, notably those of aluminium, chromium(III), and vanadyl chlorides, where reaction was very fast, the cation must be implicated in the mechanism. This conclusion was confirmed in further experiments (see Figure). The greater initial rate found with 4 mol equiv. of copper(II) chloride mixed with 4 mol. equiv. of alumin-



Effect of metal salts on chlorination of phenol by copper(II) chloride. A, Copper(II) chloride (4 mol. equiv.) and vanadyl chloride (4 mol. equiv.); B, copper(II) chloride (8 mol. equiv.); C, copper(II) chloride (4 mol. equiv.) and chromium(III) chloride (4 mol. equiv.); D, copper(II) chloride (4 mol. equiv.) and aluminium chloride (4 mol. equiv.).

ium chloride compared with the use of 8 mol. equiv. of copper(II) chloride suggests that complexes of the type CuCl₂,AlCl₃ are more powerful chlorinating agents than CuCl₂. The formation of 1:1 complexes of copper salts

8 A. S. Hay, H. W. Blanchard, G. F. Endres, and J. W. Eustance, J. Amer. Chem. Soc., 1959, 81, 6335.
⁹ I. S. Mustafin, V. N. Lenskaya, and R. K. Terekhova, Zhur.

neorg. Khim., 1963, 8, 2314 (Chem. Abs., 1964, 60, 1320).

For phenol, one cause for the accelerating effect of hydrochloric acid could be the effective removal of copper(I) chloride by complexing. Also, the increase

TABLE 3

Effect of hydrochloric acid on chlorination of phenol

Mol. equiv.	Pro	duct anal	ysis (mol	%)	para-ortho	Polymer
of HCl	o-C1	Phenol	$2, 4-Cl_2$	p-Cl	Ratio	mg
0.00	$2 \cdot 8$	69·9	Trace	27.5	9.8:1	78
1.00	2.7	69.2	Trace	$28 \cdot 2$	10.4:1	10
$2 \cdot 0$	4.1	52.7	0.6	42.6	10.4:1	0
6.0	4 ·0	38.2	0.3	57.5	14.4:1	0

in the *para-ortho* ratio with increased concentrations of hydrochloric acid suggests that the nature of the chlorinating agent is modified. Copper(II) chloride exists largely as H_2CuCl_4 in the presence of hydrochloric acid ¹² and a process involving $CuCl_4^{2-}$ as the attacking species, suggested earlier for aldehydes,² is favoured for the chlorination of phenols.

A major advantage of the use of hydrochloric acid as reaction medium, not apparent from Table 3, was that oxygen-catalysed polymerisation was greatly reduced. With sufficient hydrochloric acid, chlorinations in an atmosphere of oxygen with continuous regeneration of copper(II) chloride, and without excessive polymerisation were carried out. Under these conditions, the copper(II) chloride effectively plays the part of a catalyst for the chlorination by hydrochloric acid.

The optimum concentration of hydrochloric acid for this operation was found to be 3-5N. At higher concentrations the oxidation of copper(I) chloride was retarded, and this reaction then governed the overall rate.

¹⁰ E. V. Kiselva, Zhur. fiz. Khim., 1953, 27, 443 (Chem. Abs., 1954, **48**, 13,364).

J. M. Kochi, J. Amer. Chem. Soc., 1955, 77, 5274.
 G. Rossi and P. M. Strocchi, Gazzetta, 1948, 78, 725.

The reaction temperature could be varied widely with little effect on the overall rate. At about 70° the chlorination was rate-determining, while at 100° or over the oxidation of copper(I) chloride proceeded slowly, presumably because of the reduction in solubility of oxygen with increase in temperature. At atmospheric pressure, a temperature of 80° was found to be close to optimum for most phenols.

With reactive phenols, such as 3,5-xylenol, use of 0.5mol. equiv. of copper(11) chloride gave a fast reaction, roughly linear with time. With phenol, the use of 1 mol. equiv. of copper(11) chloride was preferred. Some results are given in Table 4.

TABLE 4

Chlorination of phenols by CuCl₂-O₂-HCl

	G.l.c. analysis of distilled product	Tar %
Phenol	(mol %)	(w/w)
Phenol	2-Cl (3.6) ; phenol (49.0) ; 2,4-Cl ₂ (0.4)	; 1.5
	4-Cl (46.9)	
		0.0

3,5-Xylenol 2-Cl (3.1); 3,5-xylenol (4.2); 2,4-Cl₂ (1.2; 3.0) 4-Cl (91.5)

6-Cl $(1\cdot8)$; o-cresol $(37\cdot8)$; 4,6-Cl₂ (trace); 4.6 2-Cresol 4-Cl (60.3)

2-hydroxybiphenyl(60); 5-chloro-2-hydr- 7.8 2-Hydroxybiphenyl * oxybiphenyl (40)

HCl and O_2 , each at 0.2 mol/h, were passed into a stirred mixture of the phenol (2 mol) and CuCl₂ (2 mol) in 5N-HCl (600 ml) for 6 h at $\$0^\circ$.

* At 90° for 14 h.

The direct chlorination of most primary aromatic amines with free chlorine results in extensive oxidation, and p-chloroaniline is normally prepared indirectly. Tertiary amines are less prone to oxidation and NN-dimethylaniline may be chlorinated directly. Chao and Cipriani¹³ investigated thoroughly the chlorination of NN-dimethylaniline with a variety of reagents, and found that the 2-chloro- and 2,4-dichloro-derivatives were the major products; 4-chloro-NN-dimethylaniline was obtained only in small amounts.

The reaction of copper(II) chloride with aromatic amines was examined. Aniline reacted rapidly with a warm aqueous solution, giving blue tars. NN-Dimethylaniline gave NNN'N'-tetramethylbenzidine on similar treatment. (This oxidative coupling by vanadium or titanium tetrachlorides has been described previously.¹⁴) However, in the presence of concentrated hydrochloric acid, the extent of oxidative side-reactions was reduced and at 100° nuclear chlorination was observed, both amines giving mainly the p-chloro-derivatives. Best results were achieved by operating in the presence of oxygen, with continuous regeneration of copper(II) chloride, and polymer formation was least when the solution was saturated with hydrogen chloride. A summary of four reactions is given in Table 5.

Stable complexes of copper(II) chloride with 2 mol. equiv. of amine or amine hydrochloride are well known 15

¹³ T. H. Chao and L. P. Cipriani, J. Org. Chem., 1961, 26, 1079. ¹⁴ W. L. Carrick and G. I. Karapinka, U.S.P. 3,322,838 (Union Carbide Corporation).

TABLE 5

Chlorination of aromatic amines by CuCl2-O2-HCl

Amine	Conditions	Conversion %	Yield %
Aniline	90° for 22 h	75	4-Cl 92·1
			2-CI I 2 4-C1 4
NN-Dimethyl- aniline	95° for 6 hr	57	4-C1 93 2-C1 1
o-Toluidine	90° for 16 h	97	4-C1 88
α -Naphthylamine	98° for 10 h	100	$2,4-Cl_2 83$ 4-Cl 5

and aniline was present in the reaction mixture as a sparingly soluble complex of 2 mol. equiv. of the amine hydrochloride with 1 mol. equiv. of copper(II) chloride. At the end of the reaction the p-chloroaniline was present in similar form and the product could be isolated by filtration followed by basification, or by basification of the whole reaction mixture. In either case it was necessary to add the mixture to an excess of base, with cooling. The reverse addition resulted in the transient liberation of free copper(II) chloride and consequent oxidation.

In hydrochloric acid, *a*-naphthylamine gave no complex with copper(II) chloride, possibly because of steric hindrance from the *peri*-hydrogen atom. The chlorination was rapid, and the dichloro-derivative was isolated by filtration of the hydrochloride from the reaction mixture.

Finally, the chlorination of anthracene in hydrochloric acid was examined. In the presence of a suitable solvent, reaction occurred readily and anthraquinone was isolated in good yield. This result recalls the similar oxidation of anthracene by bromine in aqueous dioxan.¹⁶

EXPERIMENTAL.

Gas chromatography was carried out on polypropylene sebacate colums at 175° with flame ionisation detection. Response factors were determined for the major components. N.m.r. spectra were recorded on a Varian T60 instrument.

Chlorination of 3,5-Xylenol with Copper(II) Chloride in Toluene.—Hydrated copper(11) chloride (85.2 g, 0.5 mol) was suspended in toluene (150 ml) and dehydrated azeotropically. The stirred mixture was cooled, 3,5-xylenol (24.4 g, 0.20 mol) was added, then the product was warmed from 84 to 94° over 1 h; hydrogen chloride evolution had then ceased. Copper chlorides (56.7 g) were filtered off and washed with toluene. The combined filtrate and washings were cooled in ice and crystals of 4-chloro-3,5-xylenol (m.p. 116°; 22.1 g, pure by g.l.c.) were collected, washed with light petroleum, and dried. Nearly pure 4-chloro-3,5xylenol (m.p. 115°; 7.2 g) was obtained from the mother liquor, which also contained (g.l.c.) 2-chloro-3,5-xylenol and 2,4-dichloro-3,5-xylenol; no 3,5-xylenol was detected.

Chlorination of 4-Cresol with Copper(II) Chloride in Toluene.

¹⁵ L. A. Il'yukevich and G. A. Shagisultanova, Zhur. neorg. Khim., 1963, 8, 2308 (Chem. Abs., 1964, 60, 1320); S. Prasad and P. D. Sharma, J. Inst. Chemists (India), 1958, 30, 249 (Chem. *Abs.*, 1959, **53**, 11,086). ¹⁶ C. C. Price and C. Weaver, *J. Amer. Chem. Soc.*, 1939, **61**,

3360.

-4-Cresol (108 g, 1 mol) was stirred with anhydrous copper-(II) chloride (from the hydrate, 358 g) in toluene (500 ml) for 15 hr, at 106–108°. The crude product was recovered from the toluene solution and on distillation under reduced pressure gave an oil (53 g), consisting of equal parts of 4-cresol and 3-chloro-4-hydroxytoluene, a high-boiling oil (8·3 g), and tar (47 g), non-volatile at 1 mm. The major component of the high-boiling oil was 6-chloro-4-methyl-2-(4-methyl-phenoxy)phenol, colourless prisms (3·4 g), m.p. 138° (from light petroleum) (Found: C, 68·0; H, 5·2; Cl, 15·0. C₁₄H₁₃ClO₂ requires C, 67·6; H, 5·3; Cl, 14·3%), λ_{max} (EtOH) 293 nm, λ_{max} (0·1 N-NaOH) 319 nm, τ ([²H₆]di-methyl sulphoxide) 7·80 (s, CH₃), 2·8–3·4 (m, aromatic H), and 1·0br (s, OH).

Effect of Solvent on Chlorination of Phenol by Copper(II) Chloride.—A stirred mixture of copper(II) chloride (0.20 mol) and phenol (0.10 mol) in solvent (*ca.* 30 ml) was heated, usually under reflux, in a slow stream of nitrogen until the theoretical amount of hydrogen chloride had been evolved. Copper chlorides were filtered off and the filtrate was distilled, finally under reduced pressure.

With water as solvent, the amount of copper(II) chloride was increased to 0.45 mol, in water (62 g), and the products were extracted with ether before distillation.

Effect of Metal Salts on Chlorination of Phenol by Copper(II) Chloride.—A mixture of copper(II) chloride dihydrate (13.6 g, 0.08 mol) and the metal halide (0.08 mol) in water (usually 20 ml) was stirred and heated (bath 135°) in a stream of nitrogen. Phenol (1.88 g, 0.02 mol) was added and the mixture was boiled under gentle reflux for 1 h. Water was added, which effectively stopped the chlorination, and the mixture was submitted to steam-distillation. Phenols were recovered from the distillate (40 ml) by extraction with ether and analysed as before. The aqueous residue from the steam-distillation was filtered and any solid was washed with hydrochloric acid then water, dried, and weighed. This residue is denoted as polymer in Table 2.

The results shown in the Figure were obtained by a slightly modified procedure, *e.g.* aluminium chloride $(32 \cdot 0 \text{ g}, 0 \cdot 24 \text{ mol})$ and copper(II) chloride dihydrate $(40 \cdot 9 \text{ g}, 0 \cdot 24 \text{ mol})$ were dissolved in water (150 ml) and the solution was concentrated. Hydrochloric acid (6 \cdot 2 g, 0 \cdot 06 mol) was added and the volume was adjusted to 90 ml at 90°. The solution was boiled under gentle reflux (bath 135°) and stirred in a nitrogen atmosphere. Phenol (5 \cdot 64 g, 0 \cdot 06 mol) was added. Samples of the mixture were withdrawn at intervals, diluted with water, and phenols were extracted with benzene for analysis.

Chlorination of 4-Cresol in Hydrochloric Acid.—4-Cresol (1080 g, 10 mol) and copper(11) chloride dihydrate (3410 g, 20 mol) were stirred in a mixture of concentrated hydrochloric acid (2400 ml) and water (1600 ml) at $80-82^{\circ}$ for 11.5 h while oxygen was passed through the mixture at 0.5 mol/h. Samples of the aqueous phase were withdrawn periodically and the hydrochloric content was estimated potentiometrically. Hydrogen chloride was passed into the mixture intermittently to keep the hydrochloric acid content at 3—4N. The organic product was separated from tar by steam-distillation and the resultant oil phase (950 g) was fractionally distilled using a column of 14 theoretical plates. 3-Chloro-4-hydroxytoluene (825 g, 58%) was obtained as an oil, b.p. 84° at 15 mm, of 98% purity (g.l.c.).

Oxidative Coupling of NN-Dimethylaniline.—NN-Dimethylaniline (1·2 g) was stirred at 50—60° for 2 h with a

solution of hydrated copper(II) chloride $(3\cdot4\text{ g})$ in water (10 ml). The resultant blue solid was extracted with dilute hydrochloric acid. Basification afforded a solid (0.3 g), m.p. 195° (from light petroleum), which was identical (i.r. and u.v.) with NNN'N'-tetramethylbenzidine.

Chlorination of Aniline.-Aniline (65.1 g, 0.7 mol) in concentrated hydrochloric acid (140 ml) was added to a solution of copper(II) chloride dihydrate (119 g, 0.7 mol) in fuming hydrochloric acid (700 ml). A golden solid was precipitated immediately and a small portion was removed for examination. The complex had no definite m.p., but turned black at 130° [Found: Cu, 15.5. Calc. for (C₆H₅- NH_2 , $HCl)_2$, $CuCl_2$: Cu, $16 \cdot 1\%$]. The suspension was stirred and heated at 90° for 22 h while oxygen and hydrogen chloride were passed in, each at a rate of 0.2 mol/h. The mixture was cooled in ice, and the solid was filtered off and dissolved in water (900 ml). This solution was filtered to remove a little black polymer (0.6 g), then added to an excess of ice-cold dilute ammonia solution. The precipitate of p-chloroaniline (68.1 g; m.p. 70°; 98% pure by g.l.c.) was collected, washed, and dried. Extraction of the aqueous mother liquor with ether gave an oil (15.3 g) consisting of aniline (65%), p-chloroaniline (30%), and small amounts of o-chloro- and 2,4-dichloroaniline.

Chlorination of NN-Dimethylaniline.—A slow stream of equimolar amounts of oxygen and hydrogen chloride was passed through a stirred solution of NN-dimethylaniline (12.1 g, 0.1 mol) in concentrated hydrochloric acid (50 ml) containing copper(II) chloride dihydrate (17 g, 0.1 mol) for 6 h at 95° .

The resulting clear solution was added to an excess of icecold dilute ammonia solution. The oil liberated was extracted with ether; the extract was dried (KOH) and evaporated, and the residual oil (14.6 g) was distilled under reduced pressure. The distillate (13.4 g), analysed by g.l.c., was found to contain NN-dimethylaniline (43%), o-chloro-NN-dimethylaniline (1%), and p-chloro-NN-dimethylaniline (56%).

Chlorination of o-Toluidine.—o-Toluidine (10.7 g; 0.1 mole) was chlorinated in the same way as NN-dimethylaniline, but the reaction time was extended to 16 h. Solid was present throughout the reaction. The distilled product (12.4 g, b.p. 164° at 70 mm, m.p. 28°) was found to contain (g.l.c.) o-toluidine (3%) and 4-chloro-2-methylaniline (97%).

Chlorination of a-Naphthylamine.---A slow stream of equimolar amounts of oxygen and hydrogen chloride was passed through a stirred suspension of α -naphthylamine hydrochloride (18 g, 0.1 mol) in concentrated hydrochloric acid (80 ml) containing copper(11) chloride dihydrate (17 g, 0.1 mol) for 10 h at 98°. The resulting mixture was cooled in ice; the solid was filtered off and washed with cold hydrochloric acid to remove copper chlorides, then stirred with an excess of cold ammonia solution. The liberated base was collected, washed, dried, and distilled under reduced pressure. The pale pink distillate (18.5 g, b.p. 150° at 0.5 mm) was found (g.l.c.) to contain 2,4-dichloro- α -naphthylamine (95%) and 4-chloro- α -naphthylamine (5%), with only a trace of starting naphthylamine. Recrystallisation from ethanol gave the pure dichloro-derivative, m.p. 78° (Found: C, 56·7; H, 3·4; N, 6·9. Calc. for C₁₀H₇Cl₂N: C, 56·7; H, 3·3; N, 6·6%).

Chlorination of Anthracene.—A mixture of anthracene (zone-refined; 1.78 g, 0.01 mol), copper(II) chloride dihydrate (1.7 g), diethylene glycol dimethyl ether (20 ml),

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and hydrochloric acid (50%; 10 ml) was stirred for 8 h in a stream of oxygen. The mixture was cooled and diluted with water, and the solid $(1.85 \text{ g}; \text{ m.p. } 260^\circ)$ was filtered off, washed, and dried. Crystallisation from ethanol gave anthraquinone, identical with an authentic specimen.

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