837. *Hydrolysis of Substituted* o-*Chlorobenzoic Acids. The Mechanism of the Reaction between* o-*Halogenobenzoic Acids and Nucleophilic Reagents.*

By A. A. Goldberg.

2-Chloro-4-nitrobenzoic acid is not hydrolysed in presence of a copper catalyst by aqueous sodium acetate, disodium hydrogen phosphate, or potassium carbonate at 100°, but aqueous potassium carbonate at 150° gives 4-nitrosalicylic acid. Aqueous potassium hydroxide affords high yields of 3 : 3′-dichloroazobenzene-4 : 4′-dicarboxylic acid but no 4-nitrosalicylic acid. The hydrolysis of *o*-chlorobenzoic acids by aqueous potassium carbonate appears to be general.

It is suggested that reaction between *o*-halogenobenzoic acids and nucleophilic reagents proceeds *via* a non-ionised six-membered copper chelate complex (II) and is mediated by two independent electronic displacements, so that it can only proceed in an environment which allows formation of the chelate complex. Support is adduced for this view from other reactions.

Since Ullmann (*Ber.*, 1903, **36**, 2383; 1904, **37**, 853) discovered the high reactivity of the halogen in *o*-halogenobenzoic acids towards aniline and phenol in the presence of potassium carbonate and a copper catalyst many substituted *o*-chlorobenzoic acids have been condensed with arylamines and phenols, giving various 2-carboxy-diphenylamines and -diphenyl ethers. These are important because of their convertibility into acridones and xanthones respectively. Other nucleophilic reagents such as ammonia, alkylamines, and alcohols have been successfully condensed with *o*-chlorobenzoic acids but little has been recorded on the reaction of *o*-chlorobenzoic acids with water, *i.e.*, their hydrolysis into simple salicylic acids. The present work had its origin in a search for an easy route to 4-nitrosalicylic acid which was required for the preparation of 4-aminosalicylic acid.

Ullmann (*Annalen*, 1907, **355**, 360) failed to obtain 4-nitrosalicylic acid by the action of aqueous sodium hydroxide on 2-chloro-4-nitrobenzoic acid but succeeded in effecting the hydrolysis with lime-water at 150°; the method has, however, experimental disadvantages (cf. Wenis and Gardner, *J. Amer. Pharm. Assoc.*, 1950, **38**, 9). Since salicylic acid is obtainable by the hydrolysis of *o*-bromobenzoic acid with aqueous sodium acetate (Hurtley, *J.*, 1929, 1870) it was thought desirable to examine the reaction, in the presence of a copper catalyst, of 2-chloro-4-nitrobenzoic acid with aqueous solutions of various inorganic acid-acceptors of increasing basic strength. Those selected were sodium acetate, disodium hydrogen phosphate, potassium carbonate, and potassium hydroxide. Aqueous sodium acetate, disodium hydrogen phosphate, and potassium carbonate at 100° for periods as long as 24 hours were without action. At 150°, however, aqueous potassium carbonate gave almost quantitative yields of 4-nitrosalicylic acid. The reaction appears to be generally applicable, since 2-chloro-3- and 2-chloro-5-nitrobenzoic acid yielded

respectively 3- and 5-nitrosalicylic acid, and 2 : 3-, 2 : 4-, and 2 : 5-dichlorobenzoic acids gave 3-, 4-, and 5-chlorosalicylic acid, all in high yield. Attempts to effect the hydrolysis without the use of pressure were less successful; concentrated aqueous potassium carbonate in refluxing amyl alcohol was without action; potassium carbonate in molten sodium acetate trihydrate at 130° gave only a poor yield.

With 10N-aqueous potassium hydroxide in amyl alcohol, at temperatures ranging from 95° to the reflux point (*ca.* 120°), 2-chloro-4-nitrobenzoic acid gave an almost theoretical yield of 3 : 3'-dichloroazobenzene-4 : 4'-dicarboxylic acid; no 4-nitrosalicylic acid was formed. The hydrogen necessary for the reduction of the nitro- to the azo-group apparently originates from the amyl alcohol but that this is not the entire explanation is shown by the production of the same compound, although in much smaller yield, by the action of aqueous potassium hydroxide in the absence of amyl alcohol [compare the reduction of *p*-chloronitrobenzene by sodium ethoxide in ethyl alcohol (Raiford and Colbert, *J. Amer. Chem. Soc.*, 1926, **48**, 2652) and the conversion of *m*-chloronitrobenzene by sodium methoxide into 3 : 3'-dichloroazoxybenzene (Hollemann, *Rec. Trav. chim.*, 1915, **35**, 1)]. The constitution of the dicarboxylic acid was determined by hydrogenation which, by reduction of the azo-group and simultaneous hydrogenolysis of the halogen, gave *p*-aminobenzoic acid.

The remarkable stability of the halogen substituent in 2-chloro-4-nitrobenzoic acid in the presence of the high hydroxyl-ion concentration of aqueous potassium hydroxide led to speculation on the mechanism of the general reaction between *o*-halogenobenzoic acids and anionoid reagents such as ammonia, amines, phenols, alcohols, and water, leading to ejection of the chlorine as chloride ion and its substitution by the fragment of the anionoid reagent. Ullmann (*Annalen*, 1907, **355**, 312) showed that the reaction proceeds smoothly only in the presence of traces of copper or its salts; iron, zinc, nickel, and platinum are also effective, but manganese and tin are inactive. Halogen substituents *para* to the carboxyl group do not react; for example, 2 : 4-dichlorobenzoic acid and the strongly nucleophilic *p*-anisidine give 90% yields of 2-carboxy-5-chloro-4'-methoxydiphenylamine (B.P. 353,537; Magidson *et al.*, *Chem. Pharm. Ind. U.S.S.R.*, 1935, **1**, 26; Magidson and Grigorski, *Ber.*, 1936, **69**, 396) [cf. 2 : 4-dichlorobenzoic acid with (*a*) aqueous ammonia (G.P. 244,207), (*b*) phenol (Ullmann, *Ber.*, 1904, **37**, 853), and (*c*) aqueous potassium carbonate (see below)].

The contrast between the reactivities of halogens in *o*- and *p*-halogenobenzoic acids, and the similarity of the reactivities of halogens in *o*- and *p*-halogenonitrobenzenes, is striking. It is significant that the copper catalyst, essential for the reaction between anionoid reagents and *o*-halogenobenzoic acids, is unnecessary for the reaction between the former and *o*- and *p*-halogenonitrobenzenes.

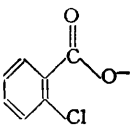
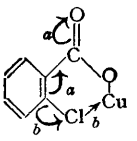
It appears that the effective initial catalyst in the reaction is a cuprous ion since cuprous iodide is an active catalyst in the presence of potassium iodide—environmental conditions under which cupric ion cannot exist (I. Goldberg, *Ber.*, 1907, **40**, 4541). Bunnett and Zahler (*Chem. Reviews*, 1951, **49**, 273) represent the catalyst as a cuprous ion which co-ordinates with the halogen, thus incipiently converting the latter into the 'onium state and increasing its replaceability in the same way as the lability of a substituted amino-group is increased by conversion into the quaternised condition (Königs and Greiner, *Ber.*, 1931, **64**, 1049; Borrows, Clayton, and Hems, *J.*, 1949, S 199); and the lability of iodine is increased by conversion into the iodonium state (Sandin *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 1550). This mechanism, however, gives no consideration to the obviously important role of the adjacent carboxyl group and the question of the functional state in which the latter group exists; nor does Bunnett and Zahler's suggestion explain the stability of halogen atoms *para* to the carboxyl group or the stability of *ortho*-halogen atoms towards potassium hydroxide.

The reaction between *o*-chlorobenzoic acids and an arylamine apparently requires the presence of a small amount of water (Goldberg and Kelly, *J.*, 1946, 102), which is normally supplied by the neutralisation of the potassium carbonate by the *o*-chlorobenzoic acid and the hydrogen chloride eliminated during the reaction. The more strongly anionoid the arylamine, the lower is the temperature at which condensation takes place. Thus, aniline requires temperatures of *ca.* 130°, and *p*-toluidine and *p*-anisidine condense readily at

100—106°; *p*-dimethylaminoaniline gives high yields at 80° (Goldberg and Kelly, *loc. cit.*); *p*-aminophenol and 2 : 4-dichlorobenzoic acid at 60° give 50% yields of 2-carboxy-5-chloro-4′-hydroxydiphenylamine (personal communication from Mr. Besly). On the other hand the weakly anionoid *p*-nitroaniline condenses with difficulty, yields of only *ca.* 18% being obtained at 180° (Albert and Linnell, *J.*, 1936, 1614).

Although the condensation of an *o*-halogenobenzoic acid and a nucleophilic reagent is carried out in presence of excess of potassium carbonate it is most improbable that the reaction proceeds *via* the ion (I) since the carboxyl ion would induce electron-accession to $C_{(2)}$ of the benzene ring, thereby inhibiting attack by anionoid reagents at this point [cf. the chlorination of aqueous sodium benzoate which gives principally *o*-chlorobenzoic acid (Saint Evre, *Ann. Chim.*, 1849, **25**, 485; Lossen, G.P. 146,174); also the effect of the first carboxyl *ion* on the dissociation constant of the second carboxyl group in the benzenedicarboxylic acids (Robinson, *J.*, 1947, 1290)]. In addition, it has been shown (see below) that the *o*-halogen substituent is completely stable in the presence of aqueous potassium hydroxide, conditions under which it would be expected that the whole of the *o*-chlorobenzoic acid would exist as the ion (I).

It is now suggested that the reaction proceeds *via* a non-ionised six-membered chelate copper complex (II) and is mediated by two independent mechanisms: (*a*) the electromeric polarisation of the system $C{=}C{-}C{=}O$, and (*b*) the polarisation of the system $C{-}Cl{\rightarrow}Cu$ in which the normal inductive effect in the $C{\dashrightarrow}Cl$ bond, and the inductometric polarisability of the bond in the presence of an attacking anionoid reagent, will be strongly augmented by the co-ordination of the chlorine with the copper. Both these processes operate in concert to create electron-defect on $C_{(2)}$ of the benzene ring, the combined total defect being sufficient to render this position easily susceptible to attack by nucleophilic reagents with consequent ejection of the chlorine as chloride ion. The polarisation (*a*) will be transmitted through the benzene ring, appearing as an electron defect at position 4; but this effect will be antagonised by, or at least not supported by, any transmission through the benzene ring of the "co-ordination polarisation" (*b*) which could only manifest itself as an electron-deficiency at position 3 or 5. The net electron-defect at position 4 will therefore be too small to initiate attack by nucleophilic reagents and accordingly halogen atoms at this position will be stable.

(I)   (II)

It would follow that environmental conditions which inhibit or suppress the Cl→Cu co-ordination bond or the O–Cu salt bond should restrain the course of the reaction. Determining conditions would be expected to be associated with the solvation and the basic strength of the acid acceptor employed. For example, potassium hydroxide is, potassium carbonate is not, soluble in amyl alcohol; accordingly it would be expected that suspensions of the latter in amyl alcohol would have no influence on the chelate complex (II) while solutions of potassium hydroxide in amyl alcohol would disrupt the C→Cl and the O–Cu bond. In addition it would be expected that excessive quantities of potassium carbonate, especially in the presence of water, would have some disruptive effect on the chelate heterocyclic system. It was therefore of interest to examine the reaction between *o*-chlorobenzoic acid and an arylamine of enhanced nucleophilic activity, *viz.*, *p*-toluidine, in amyl alcohol, with potassium carbonate and potassium hydroxide as acid acceptor. It was found that *o*-chlorobenzoic acid (1 mol.), *p*-toluidine (1·5 mols.), and potassium carbonate (2·5 equivs.) in amyl alcohol at 106° for 4 hours gave 4-carboxy-4-methyldiphenylamine in 85% yield. When the potassium carbonate was replaced by potassium hydroxide (2·5 equivs.) no reaction took place. In reactions carried out with potassium carbonate (2·5 equivs.) in amyl alcohol containing substantial amounts of water there was impairment of yield; the yield was further decreased by increasing the amount of the

carbonate (Table 1, p. 4373). Similar observations have been made regarding the action between 2 : 4-dichlorobenzoic acid and *p*-toluidine (Table 2, p. 4373).

Pertinent information is obtainable from the stability of the well-known chelate copper derivative of acetylacetone; the same underlying pattern is discernible. This substance is soluble in boiling amyl alcohol, giving a stable blue solution; on cooling, the complex crystallises unchanged. Addition of an equivalent of anhydrous or concentrated aqueous potassium carbonate effects no decomposition even on prolonged heating; excessive quantities of strong aqueous potassium carbonate effect slow decomposition; addition of one equivalent of potassium hydroxide causes immediate and complete disruption of the compound. Morgan and Drew (*J.*, 1920, 1456) record a similar stability pattern for the selenium derivative of acetylacetone.

Postulation of a chelate copper complex as the reaction intermediate is also supported by the familiar sequence of unusual and vivid colours which accompany reaction between *o*-halogenobenzoic acids and arylamines; production of striking colours is frequently diagnostic of metallic inner complex salts (Morgan and Drew, *loc. cit.*; Diehl, *Chem. Reviews*, 1937, **21**, 39).

Experimental

4-Nitrosalicylic Acid.—A solution of 2-chloro-4-nitrobenzoic acid (40·4 g., 0·2 mol.) in water (250 c.c.) and potassium carbonate (41·4 g., 0·6 equiv.) was heated with copper bronze (2 g.) and cuprous iodide (2 g.) in an autoclave at 145—150° (internal) and 75 lb./sq. in. for 8 hours without stirring. The brown liquid was diluted with boiling water, the small amount of yellow insoluble material filtered off, potassium chloride (40 g.) added, and the solution evaporated to *ca.* 300 c.c. and set aside to cool for several hours. The crystalline precipitate of potassium 4-nitrosalicylate was collected and dissolved in boiling water (100 c.c.), and the 4-nitrosalicylic acid (31·5 g.; m. p. 226—228°) precipitated by acidification to Congo-red with 10N-hydrochloric acid. Crystallisation from dilute alcohol gave the pure acid as pale yellow needles, m. p. 234° alone or mixed with a sample prepared from 4-nitroanthranilic acid (Found: equiv., 183; N, 7·8. Calc.: equiv., 183; N, 7·7%).

The yellow insoluble material, consisting of a copper complex salt of 4-nitrosalicylic acid and unchanged catalyst, was boiled with 2N-sodium hydroxide (30 c.c.) for ¼ hour and the suspension filtered. Acidification of the filtrate precipitated a further 2·0 g. of pure 4-nitrosalicylic acid.

5-Nitrosalicylic Acid.—A solution of 2-chloro-5-nitrobenzoic acid (20·2 g.) in water (500 c.c.) and potassium carbonate (20·2 g.) was heated with copper bronze (1 g.) and cuprous iodide (1 g.) for 6 hours at 155—160° (pressure 70 lb./sq. in.). The filtered solution, treated as described above, yielded 5-nitrosalicylic acid (16·2 g.), m. p. 226—228°; crystallisation from very dilute alcohol gave the pure acid (13 g.) in long needles, m. p. 234° alone or mixed with authentic material (Found: equiv., 184; N, 7·6%).

3-Nitrosalicylic Acid.—A solution of 2-chloro-3-nitrobenzoic acid (10·1 g.) in water (250 c.c.) and potassium carbonate (10·4 g.) was heated with copper bronze (0·5 g.) and cuprous iodide (0·5 g.) for 6 hours at 160°. The filtered solution was evaporated to *ca.* 170 c.c. and chilled. The yellow needles of the potassium salt were collected and dissolved in boiling water (150 c.c.), and the solution acidified to pH 2 with hydrochloric acid and kept in the refrigerator overnight. The 3-nitrosalicylic acid was collected and dried; the yield was 6·1 g., and the m. p. 146—148° alone or mixed with authentic material (Found: equiv., 184; N, 7·5%).

4-Chlorosalicylic Acid.—A solution of 2 : 4-dichlorobenzoic acid (19·1 g.) in water (500 c.c.) and potassium carbonate (20·7 g.) was heated with copper bronze (1 g.) and copper iodide (1 g.) for 12 hours at 175—180° (130 lb./sq. in.). The filtered (charcoal) solution was chilled and acidified with 10N-hydrochloric acid to pH 2, and the precipitate collected; crystallisation from 50% alcohol (280 c.c.) yielded 4-chlorosalicylic acid in long colourless needles (11·1 g.), m. p. 216—218° alone or mixed with an authentic sample (Found: equiv., 173; Cl, 20·6%. Calc.: equiv., 172·5; Cl, 20·5%).

3-Chlorosalicylic Acid.—2 : 3-Dichlorobenzoic acid (19·1 g.), treated as described for the 2 : 4-isomer, yielded 3-chlorosalicylic acid (12·3 g.), m. p. 176—178° alone or mixed with authentic material (Found, in recrystallised material, m. p. 180°: equiv., 174; Cl, 20·6%).

5-Chlorosalicylic Acid.—A solution of 2 : 5-dichlorobenzoic acid (19·1 g., 0·1 mol.) in water (500 c.c.) and potassium carbonate (20·7 g., 0·3 equiv.) was heated with copper bronze (1 g.) and cuprous iodide (1 g.) for 12 hours at 160—170°/90 lb./sq. in. The resulting filtered solution

on acidification yielded 5-chlorosalicylic acid (14·8 g.), m. p. 170°; crystallisation from dilute methanol gave the pure acid in colourless needles, m. p. 172—174° (Found: equiv., 172; Cl, 20·6%).

4-Nitrosalicylic Acid.—2-Chloro-4-nitrobenzoic acid (20·2 g., 0·1 mol.) and anhydrous potassium carbonate (20·7 g., 0·3 equiv.) were added to molten sodium acetate trihydrate (250 g.) containing copper bronze (2 g.) and cuprous iodide (2 g.) and the mixture heated to 128—135° (internal) for 8 hours; water was allowed to distil away. Boiling water (200 c.c.) was added, the solid broken up, and the suspension filtered. The solid was boiled with N-potassium hydroxide (300 c.c.) for ½ hour, the insoluble material removed, and the filtrate acidified with hydrochloric acid. Purification *via* the potassium salt gave pure 4-nitrosalicylic acid (10·2 g.), m. p. 230—232° (Found: equiv., 184; N, 7·8. Calc.: equiv., 183: N, 7·7%).

Reaction of 2-Chloro-4-nitrobenzoic acid with Aqueous-amyl-alcoholic Potassium Hydroxide: 3 : 3′-Dichloroazobenzene-4 : 4′-dicarboxylic Acid.—(a) *Reaction at* 90—95°. A solution of 2-chloro-4-nitrobenzoic acid (80·4 g., 0·4 mol.) in amyl alcohol (600 c.c.) and 10N-potassium hydroxide (100 c.c., 1 mol.) was stirred with copper bronze (5 g.) and cuprous iodide (5 g.) on the water-bath for 12 hours (internal temp. 90—95°). The amyl alcohol was distilled off in steam, the aqueous solution filtered and acidified with 5N-sulphuric acid, and the dark brown precipitate collected. This was drained and extracted for 1 hour with boiling 90% alcohol (800 c.c.) in which 2-chloro-4-nitrobenzoic and 4-nitrosalicylic acid are very soluble; the insoluble residue was a light brown powder (78 g.), m. p. >320°. This was dissolved in water and potassium carbonate monohydrate (234 g.), and the solution evaporated to small volume on the water-bath and chilled; the precipitated potassium salt (100 g.) was collected and dissolved in boiling water (300 c.c.), and the solution run into an excess of 2N-sulphuric acid stirred at 80°. The precipitate of the free acid (46 g.) was collected, washed with boiling water, and dried (Found: N, 8·1; Cl, 19·5%). It was too insoluble for purification by ordinary crystallisation but the following method of " slow precipitation-crystallisation " was effective. A solution of the acid (46 g.) in boiling water (400 c.c.) and pyridine (125 c.c.) was stirred at the b. p. and hot 5N-sulphuric acid added dropwise very slowly until the pH value was 4·0. *3 : 3′-Dichloroazobenzene-4 : 4′-dicarboxylic acid* separated as a cream-coloured microcrystalline powder (27 g.), m. p. 356° (Found: equiv., 171; C, 49·2; H, 2·2; N, 8·3; Cl, 20·7. $C_{14}H_8O_4N_2Cl_2$ requires equiv., 169·5; C, 49·5; H, 2·4; N, 8·3; Cl, 20·9%). Further acidification of the aqueous pyridine filtrate to pH 2·0 gave another 9 g. of the acid, m. p. 356° (Found: equiv., 170; N, 8·2; Cl, 20·6%).

(b) *Reaction at* 130°. 2-Chloro-4-nitrobenzoic acid (80·4 g., 0·4 mol.), amyl alcohol (500 c.c.), 10N-potassium hydroxide (100 c.c., 1 mol.), copper bronze (5 g.), and cuprous iodide (5 g.) were stirred together at the b. p. for 3 hours during which solvent (500 c.c.) was allowed to distil off, being replaced at regular intervals by a total of 400 c.c. of amyl alcohol. The mixture was then stirred at the b. p. for a further 4 hours. Isolation of the product as described above and extraction with boiling alcohol left 3 : 3′-dichloroazobenzene-4 : 4′-dicarboxylic acid (71 g.), m. p. >330°. Purification *via* the pyridine salt yielded pure acid (47 g.), m. p. 354°. A recrystallised sample had m. p. 356° (Found: equiv., 170·5; N, 8·4; Cl, 20·5%).

The following derivatives of 3 : 3′-dichloroazobenzene-4 : 4′-dicarboxylic acid were made: *acid chloride*, orange rosettes (from toluene), m. p. 120—122° (Found: N, 7·3; Cl, 37·4. $C_{14}H_6O_2N_2Cl_4$ requires N, 7·5; Cl, 37·8%); *ethyl* ester (from the chloride and alcohol), orange needles (from alcohol), m. p. 88° (Found: N, 7·3; Cl, 18·2. $C_{18}H_{16}O_4N_2Cl_2$ requires N, 7·1; Cl, 18·0%); *amide* (from the chloride and aqueous ammonia), orange needles (from pyridine–dioxan–water), m. p. 330° (Found: N, 16·5; Cl, 20·8. $C_{14}H_{10}O_2N_4Cl_2$ requires N, 16·6; Cl, 21·0%); p-*chloroanilide*, orange needles (from aqueous pyridine), m. p. 330—332° (Found: N, 9·9; Cl, 25·4. $C_{26}H_{16}O_2N_4Cl_4$ requires N, 10·0; Cl, 25·4%).

Hydrogenation of 3 : 3′-Dichloroazobenzene-4 : 4′-dicarboxylic Acid.—The foregoing acid (3·4 g., 0·01 mol.) was dissolved in water (100 c.c.) and 2·5N-sodium hydroxide (15 c.c.), and 2·5N-acetic acid added until the pH was 8·3. 5N-Sodium hydroxide (5·0 c.c.) was added and the orange solution hydrogenated over Raney nickel at 20°/760 mm. Uptake of hydrogen was rapid (865 c.c. at N.T.P. in 2½ hours; no more after another 3 hours) (Calc. for reduction of azo- to amino-group with simultaneous dehalogenation: 896 c.c.). The catalyst was filtered off and washed with the filtrate; the colourless solution required 10·3 c.c. of 0·5N-sulphuric acid for adjustment to pH 8·3. Accordingly the amount of 5N-sodium hydroxide neutralised by the hydrogen chloride generated was 4·0 c.c. (Calc. for elimination of 2HCl per mol.: 4·0 c.c.). Dilute sulphuric acid was added until the pH was 4·0; the solution (250 c.c.), kept at 0° for 24 hours, deposited needles (1·4 g.) of *p*-aminobenzoic acid, m. p. 188—190° alone or mixed with

authentic material (Found: equiv., 137; N, 10·4. Calc.: equiv., 137; N, 10·2%). Electrometric analysis showed that the filtrate contained a total of 0·65 g. of chloride ion (Calc.: Cl^-, 0·71 g.).

Reactions between o-*Chloro- and* 2 : 4-*Dichloro-benzoic Acid and* p-*Toluidine with Potassium Carbonate or Potassium Hydroxide as Acid-acceptor.*—The method used is exemplified by the following. To *o*-chlorobenzoic acid (39·1 g., 0·25 mol.) in amyl alcohol (337 c.c.) potassium carbonate (43 g., 0·625 equiv.) was added during ¼ hour, with stirring, at *ca.* 50°. Copper bronze (2 g.), cuprous iodide (2 g.), and *p*-toluidine (40·1 g., 0·375 mol.) were added and the mixture stirred at 104—106° (internal) for the stated time; no solvent was allowed to distil away. The amyl alcohol was removed in steam, the residual solution filtered, evaporated to a standard volume, and acidified with 5N-sulphuric acid to pH 4, and the 2-carboxy-4′-methyldiphenylamine filtered off. The filtrate was further evaporated and acidified to pH 2, then chilled, and the recovered *o*-chlorobenzoic acid collected. The aqueous filtrate was adjusted to a suitable volume and an aliquot analysed for chloride ion by electrometric titration with Ag/Pb–Hg electrodes. The 2-carboxy-4′-methyldiphenylamine and recovered *o*-chlorobenzoic acid were, when necessary, recrystallised until the m. p. was within 4° of the correct value and the identity of the products in all cases checked by mixed m. p.s and molecular-weight determination. For results see Tables.

TABLE 1. *Reaction between* o-*chlorobenzoic acid* (1 *mol.*) *and* p-*toluidine* (1·5 *mol.*) *at* 106°

Acid-acceptor K_2CO_3 (equiv.)	Acid-acceptor KOH (equiv.)	Time (hours)	Amyl alcohol (c.c.)	Water (c.c.)	Cl^- liberated (g.-ion)	Yield [a] (mol.)	Recovered acid (mol.)
2·5	—	4	1350	—	1·04	0·85	—
2·5	—	8	1350	225	0·33	0·15	0·60
2·5	—	16	1350	225	0·48	0·35	0·55
2·5	—	24	1350	225	0·80	0·50	0·22
5·0	—	4	1350	—	0·99	0·72	—
5·0	—	4	1350	225	0·32	0·08	0·65
10·0	—	4	1350	—	0·15	0·05	0·70
10·0	—	4	1350	225	0·10	—	0·82
—	2·5	4	1350	—	0·02	—	0·92
—	2·5	16	1350	—	0·04	—	0·88
—	2·5	6	1350	225	0·02	—	0·87
—	2·5	16	1350	225	0·02	—	0·86

[a] 2-Carboxy-4-methyldiphenylamine.

TABLE 2. *Reaction between* 2 : 4-*dichlorobenzoic acid* (1 *mol.*) *and* p-*toluidine* (1·5 *mol.*) *at* 106°.

Acid-acceptor K_2CO_3 (equiv.)	Acid-acceptor KOH (equiv.)	Time (hours)	Amyl alcohol (c.c.)	Water (c.c.)	Cl^- liberated (g.-ion)	Yield [b] (mol.)	Recovered acid (mol.)
2·5	—	4	1350	—	1·02	0·94	—
—	2·5	4	1350	—	0·04	—	0·93
—	2·5	4	1350	225	—	—	0·96

[b] 2-Carboxy-5-chloro-4′-methyldiphenylamine.

Action of Potassium Carbonate and Potassium Hydroxide on the Copper Acetylacetone Salt.—(*a*) A solution of the copper derivative (1·0 g.) of acetylacetone in amyl alcohol (75 c.c.) was heated on the water-bath for 4 hours. On cooling, 0·84 g. of the complex separated in long blue needles. (*b*) A solution made as described above and heated with 2·5 c.c. of water and 0·7 g. of potassium carbonate on the water-bath for 4 hours gave a similar result. (*c*) A solution made as described above and heated with 10 c.c. of water and 2·5 g. of potassium carbonate for 4 hours on the water-bath gave a similar result. (*d*) Repetition of (*c*) with 6 g. of potassium carbonate gave 0·44 g. of recovered copper salt; the potassium carbonate layer was very dark brown. (*e*) To a solution of the copper salt (1·0 g.) in hot amyl alcohol (75 c.c.) was added potassium hydroxide (0·7 g.) in amyl alcohol (10 c.c.). The solution instantly became dark brown; on cooling, no copper salt separated.

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