XXXIX.—*The Chlorination of Phthalic Acid in Alkaline Solution.*

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THE chlorination of phthalic acid in alkaline solution, first described by Auerbach (*Chem.-Ztg.*, 1880, **4**, 407) and confirmed by Zincke and Schmidt (*Ber.*, 1894, **27**, 741), was shown by Egerer and Meyer (*Monatsh.*, 1913, **34**, 81) to yield 4-chlorophthalic acid. Moore, Marrack, and Proud (J., 1921, **119**, 1788), in preparing the latter by this method, could not obtain it sufficiently pure for analysis. From the divergence in the analyses and constants given by the above workers for the chloro-acid and its anhydride, and also from their disagreement with the values obtained for these compounds, when prepared by other methods (compare Beilstein, "Handbuch der Organische Chemie," IV Aufl., IX, 816; Bogert and Renshaw, *J. Amer. Chem. Soc.*, 1908, **30**, 113; von Braun, *Ber.*, 1923, **56**, 2332), it would appear that the pure acid cannot be readily obtained by the direct chlorination method. It seemed of interest, therefore, to submit the method to a closer investigation.

The chlorination proceeds most satisfactorily with 3 molecules excess of potassium hydroxide. The precipitated potassium hydrogen salts consist mainly of 4-chlorophthalate together with a little phthalate and some 4 : 5-dichlorophthalate, which has not been previously recognised in this reaction and was identified through the anhydride. The earlier workers (Auerbach; Egerer and Meyer;

Zincke and Schmidt, *locc. cit.*) give no clue as to the excess of alkali employed, and Moore, Marrack, and Proud (*loc. cit.*) recommend the use of 5 molecules excess of sodium hydroxide. This quantity, however, was found to yield a product containing a much larger proportion of dichlorophthalate, which could not be removed entirely by the methods of purification recommended, and its presence would account for the observation of Moore, Marrack, and Proud that chloride is retained, and for the high chlorine content of the 4-chloro-anhydride found by Egerer and Meyer.

The separation of 4-chlorophthalic acid from admixed phthalic and 4 : 5-dichlorophthalic acids by means of solvents, as recommended by previous workers, was not found practicable owing to the small difference in solubility of the chloro-acids. Conversion of the mixed acids into their methyl esters, however, gave a mixture which was readily separated by distillation under reduced pressure, the methyl 4-chlorophthalate obtained yielding pure 4-chlorophthalic acid, m. p. 151°.

The formation of the chlorophthalic acid by this method has been ascribed (Egerer and Meyer, *loc. cit.*) to the action of the hypochlorite first formed. This type of action, however, is generally associated with amines, acid amides and imides, and hydroxy-compounds only. Hypochlorite solution has no action on a neutral phthalate solution, whereas chlorine yields chlorophthalates, the yield of precipitated salts being, however, small, the greater portion of the chlorophthalates remaining in solution. The chlorination, therefore, is not dependent on the presence of the excess of alkali but results from the direct action of chlorine upon the phthalate in solution. The larger yields of precipitated acid salts obtained when excess of alkali is used show that the latter serves for the ready isolation of the chlorinated products, which are salted out by the alkali chloride formed. This view is supported by the different results obtained with sodium hydroxide and potassium hydroxide. Comparative experiments show that the chlorinated product contains much more dichlorophthalate when the former is used, and this difference, which has not been previously observed, can only result from solubility differences. Potassium hydrogen 4-chlorophthalate can only be sparingly soluble under the experimental conditions and is precipitated before much dichlorination can take place, whereas the sodium hydrogen 4-chlorophthalate must be more soluble, remaining in solution while further chlorination occurs.

EXPERIMENTAL.

Chlorination of the Alkaline Phthalate Solution.—A rapid stream of chlorine was passed into an ice-cooled solution of 16·6 g. of phthalic acid in 200 c.c. of water containing 28 g. of potassium hydroxide (3 mols. excess) until no apparent further precipitation of acid potassium salt occurred; on standing, a small additional quantity separated (total yield, 19 g. or 80%). The acid salt was dissolved in 40% sulphuric acid, and the solution extracted with ether, the extract yielding the crude acid, m. p. 141—150° (Found: equiv. by titration with baryta, 99·6. Calc., 100·25). Examination of the crude acid (*a*) by fractional precipitation from aqueous solution by means of hydrochloric acid (compare Crossley and Renouf, J., 1906, **89**, 1552), (*b*) by fractional extraction with benzene (compare Auerbach; Egerer and Meyer, *locc. cit.*), and (*c*) by conversion into the anhydride by means of acetyl chloride and fractional crystallisation of the anhydride from carbon tetrachloride, failed to yield a monochloro-compound free from dichloro-. Under (*a*) and (*b*) phthalic acid was the least soluble, and under (*c*) the least soluble fractions ultimately yielded 4 : 5-dichlorophthalic anhydride, m. p. 187° (compare Villiger, *Ber.*, 1909, **42**, 3532) (Found: Cl, 32·8. Calc.: Cl, 32·7%). This m. p. was unchanged by admixture with 4 : 5-dichlorophthalic anhydride prepared from 4 : 5-dichloro-*o*-xylene (Hinkel, Ayling, and Bevan, J., 1928, 1876).

Separation by the Esterification Method.—The crude chloro-acid, m. p. 141—150°, was esterified in the usual manner with methyl alcohol and hydrogen chloride, the excess of alcohol removed under reduced pressure, and the residue poured into water. Extraction with ether yielded a thick liquid which only solidified to a white mass on cooling in a freezing mixture. Distillation under reduced pressure yielded methyl 4-chlorophthalate, b. p. 186—187°/32 mm., which solidified when cooled with ice and crystallised from well-cooled light petroleum (b. p. 40—60°) in fine white needles, m. p. 38° (Rée, *Annalen*, 1886, **233**, 236; Graebe and Rée, J., 1886, **49**, 527, give 37°) (Found: Cl, 15·6. Calc.: Cl, 15·5%).

Hydrolysis of the methyl 4-chlorophthalate by the usual method yielded 4-chlorophthalic acid, m. p. 151°, unchanged by recrystallisation from carbon tetrachloride or benzene (von Braun, *loc. cit.*, gives 157° for the acid obtained from ethyl 4-chlorophthalate) (Found: Cl, 17·5. Calc.: Cl, 17·7%). No retention of solvent was observed and it is possible that the observation of Moore, Marrack, and Proud (*loc. cit.*) was due to the acetic acid used in conjunction with the benzene.

4-Chlorophthalic anhydride, obtained from the acid by means of acetyl chloride, crystallised from carbon tetrachloride in small plates, m. p. 97° (Found: Cl, 19·7. Calc.: Cl, 19·5%).

Comparative Experiments with Sodium and Potassium Hydroxides.—Chlorine was passed simultaneously through two solutions each of 16·6 g. of phthalic acid in 200 c.c. of water, containing 24 g. of sodium hydroxide (4 mols. excess) in the one case and 33·6 g. of potassium hydroxide (4 mols. excess) in the other. The chlorination and the isolation of the crude acid were carried out as described above.

	NaOH expt.	KOH expt.
Yield of acid salt	19·9 g.	16·3 g.
Calc. for monochlorophthalate	22·25 g.	23·85 g.
Mol. wt. of acid salt (by baryta)	243·1	240·2
Calc. for monochlorophthalate	222·5	238·5
M. p. of crude acid	153—156°	145—148°
Equivalent of acid (by baryta)	107·3	100·0

Monochlorophthalic acid requires : m. p. 151°; equiv. 100·25.

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