Anal. Subs., 0.3356, 0.2838; cc. of 0.1062 *N* alkali, 43.69, 36.73. Calcd. for $C_6H_8O_4$: equivalent weight, 72. Found: 72.3, 72.7.

The necessity for the removal of the ester was shown by the high neutral equivalent value of 85 which was obtained when the step was omitted.

Summary

Mandelic acid undergoes an esterification process at 200° or below into PhCHOHCO—O—$(CHPhCOO)_n$—CHPhCOOH but the pyrolysis into diphenylmaleic anhydride and phenylacetic acid at 250° is best explained by assuming the transitional, concurrent existence of dimandelic anhydride. This is similar to the known transformation of benzilic acid into dibenzilic anhydride (benzilide). The other products from mandelic acid at 250° are water, benzaldehyde, carbon dioxide and carbon monoxide.

Ethyl dimandelate, dimandelic acid hydrate and dimandelic anhydride were synthesized. Dimandelic anhydride pyrolyzed at 250° in the manner of mandelic acid. A preliminary study was made of dilactic anhydride.

Cyclohexylglycolic acid decomposed at 250° into carbon monoxide and hexahydrobenzaldehyde, presumably through intermediate esters of the type mentioned with mandelic acid. In contrast to mandelic acid, the yield of carbon dioxide was small and there was no evidence for the formation of acid anhydrides as intermediate products.

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Certain Dichloronaphthalenes and Related Intermediates

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Although all of the ten dichloronaphthalenes have long been known, the literature contains a remarkably small amount of information regarding their preparation and properties. The present research was undertaken to produce 50–100 g. samples of 1,2-, 1,4-, 1,5- and 2,6-dichloronaphthalenes in a high state of purity.

The methods recorded in the literature for making the intermediates and the dichloro compounds are given in too little detail to be of any great help in this work. In each case various suggestions obtained from the literature were tested and modified until combinations of real preparative value were developed. The processes evolved represent an unusual amount of laborious experimentation and consequently are recorded in some detail.

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Experimental

Preparation of the Chloronaphthalene Sulfonates.—The starting materials for most of the present work were the following commercial intermediates,[2] all aminonaphthalene sulfonic acids with the groups in the positions indicated. Naphthionic acid (1,4); Laurent's acid (1,5); 1,6-Cleve's acid (1,6); 1,7-Cleve's acid (1,7); Peri acid (1,8); Brönner's acid (2,6); F-acid (2,7); and Badische acid (2,8). These were dissolved in alkali, filtered, precipitated by acid and diazotized by the addition of solid sodium nitrite in the presence of excess hydrochloric acid. Any excess of nitrous acid was destroyed by urea. The suspension of the solid diazonium compounds was added with stirring to an excess of cuprous chloride solution in hydrochloric acid. In the first part of the work the resulting mixture was evaporated to dryness. Since the reactions were carried out in 20-liter quantities, this was laborious and troublesome because of the large amounts of hydrogen chloride evolved. The result was a dry mixture of the desired sodium chloronaphthalene sulfonate with inert sodium and copper salts which could be treated directly with phosphorus pentachloride to make the sulfonyl chloride. It was later found that the addition of large amounts of sodium chloride to the mixture after the Sandmeyer reaction precipitated the sodium chloronaphthalene sulfonate, contaminated only by sodium chloride. This was dried and treated with phosphorus pentachloride. The 1,4- and 2,7-compounds precipitated from the reaction mixtures without the addition of sodium chloride. The others had to be salted out. Typical preparations follow.

Sodium 1-**Chloronaphthalene-5-sulfonate** (Evaporation **Method**).—A solution of 440 g. of Laurent's acid in 1 liter of solution containing 80 g. of sodium hydroxide was placed in a 20-liter crock stirred mechanically and treated with 500 cc. of water and 1 kg. of crushed ice, followed by 1 liter of 28% commercial hydrochloric acid. Crushed ice was added when necessary to keep the mixture below 5°. The suspension was stirred and diazotized at 0 to 5° by the addition of 135 g. of powdered sodium nitrite during eight hours. A small amount of urea was added to remove excess nitrous acid. In another 20-liter crock 1 liter of a solution of 2 mols of cuprous chloride in hydrochloric acid was stirred while the diazotized mixture was added to it. A vigorous evolution of nitrogen followed. The mixture was allowed to stand overnight and then evaporated in large dishes on steam-baths with mechanical stirring and the aid of air jets directed across the surface. The solid residue was powdered and dried in an oven at 110–120°. The gray powder obtained weighed 985 g.

Sodium 1-**Chloronaphthalene-6-sulfonate** (**Salting-out** **Method**).—A similar run with 800 g. of 1,6-Cleve's acid was carried through the treatment with cuprous chloride. The solution was then filtered from a small amount of insoluble material and treated with 1.5 kg. of sodium chloride with stirring. The sodium sulfonate precipitated, was filtered off and air-dried to constant weight at 70°; yield 490 g.

Preparation of the Chloronaphthalene Sulfonyl Chlorides.—The nine sulfonyl chlorides of the present study were all made as follows: in a large mortar previously heated on a steam-plate an excess of phosphorus pentachloride was quickly powdered (hood) and ground vigorously with the dry powdered crude sodium sulfonate. Heat was evolved and the mixture became fluid. When the reaction was complete the grinding was stopped and the mixture was allowed to stand overnight. The hard crystalline mass was then broken up and added carefully to an excess of cracked ice. After washing by decantation, the crude sulfonyl chlorides were ground with water in the mortar to remove any unchanged halides of phosphorus. After air drying, the crude sulfone chlorides were extracted in large funnel extractors[3] with boiling ligroin (60–90°). The

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(2) Most of these materials used were supplied by the Dyestuffs Department of E. I. du Pont de Nemours & Co., through its Jackson Laboratory.

(3) "Organic Syntheses," 1922, Vol. II, p 49.

cooled extract gave crystals which could be further purified by crystallization from ligroin, carbon tetrachloride or glacial acetic acid. The results with the sulfonates and sulfonyl chlorides are summarized in Table I.

TABLE I

PREPARATION OF CHLORONAPHTHALENE SULFONYL CHLORIDES

Intermediate[a]	$ClC_{10}H_6SO_3Na$, g. made	$ClC_{10}H_6SO_2Cl$ Groups	Yield,[c] %	M. p.
Na naphthionate	2473[b]	1,4	70	92–93
Laurent's acid	5215[d]	1,5	30	
Cleve's acid, 1,6	1351[e]	1,6	60	111–112
Cleve's acid, 1,7	1636[e]	1,7	45	92–92.5
Peri acid	3937[d,f]	1,8	30	96–98
Peri acid	4085[e]			
$2\text{-}NH_2C_{10}H_6SO_3Na\text{-}1$	582[g]	2,1	50	74–75
Brönner's acid (68%)	3139[d]	2,6	30	109
F-acid	291[b]	2,7	60	84.5–85
Badische acid	368[e]	2,8	[h]	129

[a] In most cases several runs were made. The weights of intermediates used were nearly equal to the weights of salts obtained. [b] Sodium salt precipitated spontaneously. [c] Yield based on crude salts used. [d] Mixture of Na and Cu salts evaporated to dryness. [e] Na salt precipitated by adding solid sodium chloride with stirring. [f] This salt mixture could not be dried above 100° without some decomposition. [g] This salt could not be dried above 70° without decomposition. [h] The 2,8 sulfonyl chloride was obtained only by heating the crude sodium salt with phosphorus pentachloride at 120–130°.

The following sulfonyl chlorides were similarly prepared: naphthalene-1-sulfonyl chloride, m. p. 65–66.5°, 449 g., 66% yield; naphthalene-2-sulfonyl chloride, m. p. 76–77°, 1315 g., 64% yield; naphthalene-2,7-disulfonyl chloride, m. p. 156–157°, 600 g., 42% yield.

Preparation of the Dichloronaphthalenes.—The preparation of the 1,4 compound is typical. In a 500-cc. flask fitted with a wide reflux condenser 52 g. of 1-chloronaphthalene-4-sulfonyl chloride (1 mol) and 125 g. (3 mols) of phosphorus pentachloride were heated in an oil-bath at 160–165° for five hours. The mixture was cautiously poured on a large amount of cracked ice. The gray liquid solidified when washed with water. The crude solid was ground with water, dried and extracted with 200 cc. of alcohol. The hot extract was treated with decolorizing carbon, filtered and diluted with water to a slight turbidity. On cooling, long white needles separated, m. p. 67–68°, 19 g., 49% yield. A run using 418 g. of the sulfonyl chloride gave 150 g. of 1,4-dichloronaphthalene, m. p. 67.4–68°. In a similar way the following dichloronaphthalenes were prepared: 1,5-, 97 g., m. p. 106–107°, 36% yield; 1,2-, 112 g., b. p. 295–298°, m. p. 33–34°, 36% yield; 2,6-, 52 g., m. p. 136°, 45% yield.

Summary

1. The preparation of four of the dichloronaphthalenes and of nine of the chloronaphthalene sulfonyl chlorides has been developed on a large laboratory scale.

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