Amide Derivatives of the Isomeric Dichlorobenzoic Acids

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The preparation of the anilides and *p*-toluides of the six isomeric dichlorobenzoic acids is described. Properties of these amides are reported along with a preparation of 2,3-dichlorobenzoic acid.

ALTHOUGH the isomeric dichlorobenzoic acids have been known for some time (*1, 3, 5*), identification has been rather difficult because only a few solid derivatives have been reported. Hubner (*2*) and Waters (*6*) have listed the melting points of 2,5-dichlorobenzanilide and 3,5-dichlorobenzanilide, respectively. The melting points reported in the literature are not in agreement with the values determined during this present work. Mather (*4*) has prepared the anilides of all six isomers during the course of a kinetic study, but the melting points were not reported.

Since 2,3-dichlorobenzoic was not available commercially, a detailed preparation of this compound is included. Our synthesis is based on a general outline indicated by Mather (*4*).

EXPERIMENTAL

Preparation of 2,3-Dichlorobenzoic Acid. 2,3-Dichloroaniline was diazotized by treating a solution of 27 grams of the amine in hydrochloric acid at 0° C. with a cold aqueous solution containing 22 grams of sodium nitrite. Copper (I) cyanide was prepared by reducing 75 grams of copper sulfate pentahydrate with 21 grams of sodium bisulfite in the presence of a few drops of sulfuric acid, followed by reaction with a solution containing 21 grams of potassium cyanide. The copper (I) cyanide was filtered, washed with hot water, and dissolved with 30 grams of sodium cyanide in 74 ml. of water. The cyanide solution was warmed to 70° C. before the diazotized 2,3-dichloroaniline was added. After refluxing for 1.5 hours, the 2,3-dichlorobenzonitrile was recovered by steam distillation. Hydrolysis of the nitrile was effected by refluxing in 60% sulfuric acid for 1.5 hours. The acid was recovered by pouring the cooled hydrolysis mixture into ice water. The crude acid, 14.9 grams (47%), was purified by crystallization from petroleum ether, b.p. 90-98° C., giving a product melting at 170-172° C. Calcd. for $C_7H_4O_2Cl_2$: C, 43.98; H, 2.11; N.E., 191. Found: C, 44.50; H, 2.24; N.E., 189.

Preparation of the Anilides and *p*-Toluides of Dichlorobenzoic Acids. The acid was converted to the corresponding acid chloride by refluxing 4 ml. of thionyl chloride, 2 drops of pyridine, and 1 gram of acid for 45 minutes. Excess thionyl chloride was then removed under vacuum. A benzene solution of the acid chloride was refluxed for 10 minutes with a benzene solution of aniline or *p*-toluidine. A ratio of 0.5 gram of acid chloride to 1.5 grams of amine generally yielded 0.5 to 0.6 gram of amide. After being refluxed, the insoluble amine hydrochloride was removed by filtration and the filtrate washed successively with dilute acid, water, dilute base, and water. After evaporation of the benzene, the derivatives were crystallized from dilute ethanol or petroleum ether, b.p. 90-98° C.

The melting points of the acids and the amides are reported in Table I.

Table I. Anilides and *p*-Toluidides of Dichlorobenzoic Acids

		Analysis, %^{a}			
		C		H	
Compound	M.P., ° C.	Calcd.	Found	Calcd.	Found
2,3-Dichlorobenzoic acid	172–5^b				
Anilide	153^c	58.67	58.50	3.41	3.67
p-Toluide	147–148^c	60.02	60.29	3.96	4.04
2,4-Dichlorobenzoic acid	164.3				
Anilide	153–154.5	58.67	58.75	3.41	3.68
p-Toluidide	168	60.02	60.07	3.96	4.18
2,5-Dichlorobenzoic acid	155				
Anilide	138–139	58.67	58.91	3.41	3.62
p-Toluidide	151–152	60.02	60.24	3.96	3.98
2,6-Dichlorobenzoic acid	144				
Anilide	177–178	58.67	58.87	3.41	3.27
p-Toluidide	222–223^c	60.02	60.13	3.96	3.87
3,4-Dichlorobenzoic acid	211–212				
Anilide	182–183	58.67	58.70	3.41	3.65
p-Toluidide	186	60.02	60.05	3.96	4.20
3,5-Dichlorobenzoic acid	188^c				
Anilide	152–153	58.67	58.91	3.41	3.34
p-Toluidide	175–176	60.02	60.04	3.96	4.12

[a] Analyses run by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [b] Sublimed. [c] Recrystallized from petroleum ether, b.p. 90-98° C.; all others recrystallized from dilute ethanol.

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