

In general, the solubility of all the salts is of the same order. They are readily soluble in warm water, warm alcohol and warm acetic acid, but are much less soluble in a dilute solution of the acid from which they were formed. A number of the salts have distinct colors when freshly recrystallized (usually a pink tint) due to water of crystallization. The color disappears on drying the salt at 110°.

Veratrylphenylethylamine and homoveratrylphenylethylamine failed to demethylate normally with hydriodic acid. The products formed are being examined.

The melting points above cited are corrected. Boiling points were taken on Anschütz thermometers. The author is indebted to Mr. Walter S. Ide for the majority of the micro analyses in this paper.

Summary

A series of 3,4-dihydroxybenzyl- β -phenylethylamines and 3,4-dihydroxydi-(β -phenylethyl)-amines is described, together with the intermediate Schiff bases and secondary amines.

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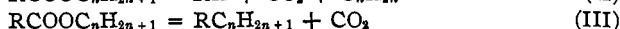
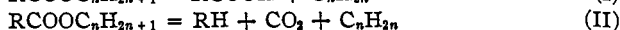
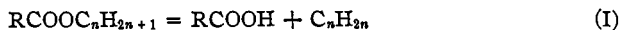
CATALYSIS IN ORGANIC CHEMISTRY. IV. DECOMPOSITIONS OF ESTERS AND ACIDS BY ANHYDROUS ZINC CHLORIDE

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The types of decomposition of esters by anhydrous zinc chloride described in a previous paper¹ may be represented by the equations



The transformation of ethyl benzoate into benzoic acid, benzene and ethylene and the conversion of methyl salicylate into *o*-cresol and carbon dioxide are typical decompositions. It has been noted that diethyl oxalate and succinate react with anhydrous zinc chloride, yielding ethyl chloride and zinc salts. The present paper gives an account of the behavior of twelve esters and seven acids.

Discussion of Experiments

Pure freshly distilled or crystallized esters or acids and 0.5 mole of anhydrous zinc chloride per mole of ester or acid were used. Unless otherwise stated, the decomposition products were isolated by the proced-

¹ Underwood and Baril, *THIS JOURNAL*, 52, 395 (1930).

ures described in a previous paper.¹ The results of our experiments with esters are given in Table I.

TABLE I
RESULTS WITH ESTERS

Carbon dioxide was evolved in all the decompositions except that of benzyl acetate. In the calculation of yields of products allowance was made for the ester recovered. The volatile unsaturated hydrocarbons were collected as dibromides. No evidence of decomposition was found in experiments with diethyl carbonate and ethyl *m*-nitrobenzoate.

No.	Ester	Moles	Time of heating, hours	Products				Type of decomp.	
				Hydrocarbon	Unchanged %	Acids and other products	%		
1	Ethyl chlorocarbonate	0.4	"	Ethylene	17.7	25.3	Ethyl chloride Hydrogen chloride	25.7	II, III
2	<i>n</i> -Propyl chlorocarbonate	.2	"	Propylene	5.5		<i>n</i> -Propyl chloride Hydrogen chloride	23.0	II, III
3	Diethyl carbonate	.2	3			95.0			
4	Di- <i>n</i> -butyl carbonate	.125	2	Butene (1)	19.3	4.6	<i>n</i> -Butyl alcohol ^{b,c}	94.8	II
5	Isopropyl benzoate	.25	2	Propylene	15.2		Benzoic acid ^b	68.8	I, II
				Benzene ^{b,d}	22.8		Isopropyl chloride ^{b,d}	22.0	
6	Di- <i>n</i> -butyl phthalate	.4	2	Butene (1)	18.0	5.4	Phthalic acid ^{b,e} Phthalic anhydride ^{b,e} Benzoic acid ^b <i>Sec.</i> -butyl alcohol ^{b,e} <i>n</i> -Butyl chloride ^e Phenol ^b	20.6 9.0 5.5 44.1 7.7 72.9	I, II
7	Isoamyl salicylate ^f	.125	2	Isopropyl-ethylene Dimer of isopropyl-ethylene	7.2 3.6		High-boiling residue, 5 g. <i>o</i> -Toluidine ^{b,g} <i>o</i> -Ethylaniline ^h		II
8	Methyl anthranilate	.1	1					75.0	III
9	Ethyl anthranilate	.05	1.5					66.0	III
10	Diethyl ester of methylmalonic acid ⁱ	.1	1	Ethylene	6.5	23.0	Ethyl propionate ^{b,i} Acetic acid ^{b,j}	63.6 96.0	II I
11	Benzyl acetate ^j	.2	2						
12	Ethyl <i>m</i> -nitrobenzoate ^k	.125	3			91.0			

^a The mixture of the ester and anhydrous zinc chloride evolved gases spontaneously until none of the liquid was left in the flask; a 50% aqueous solution of pyridine was used to absorb the hydrogen chloride. The decomposition of ethyl chlorocarbonate has been noted previously by Butlerow [*Bull. soc. chim.*, 586 (1863)] and Ulsch [*Ann.*, **226**, 281 (1884)]. ^b The tests described by Mulliken ["Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, 1916, 1922, Vols. I, II and IV] were used for the identification of this compound. ^c The liquid secured by distillation of the reaction mixture was fractionated three times. ^d Evidently zinc chloride converts some of the benzoic acid formed by the decomposition of the ester into benzene and carbon dioxide. The presence of isopropyl chloride in the reaction products indicates that zinc chloride reacted with some of the isopropyl benzoate. ^e The phthalic anhydride sublimed in the neck of the flask and was removed before the reaction mixture was distilled. Phthalic and benzoic acids were separated by means of cold chloroform. Evidently anhydrous zinc chloride splits the ester into phthalic acid and butylene; the water formed in the transformation of some of the phthalic acid into the anhydride converts some of the butylene into *sec.*-butyl alcohol. The presence of *n*-butyl chloride in the products indicates that zinc chloride reacted with a small amount of di-*n*-butyl phthalate. ^f Apparently isoamyl salicylate does not undergo the previously noted type of decomposition¹ which converts methyl and ethyl salicylates into *o*-cresol and *o*-ethylphenol, respectively. ^g The reaction mixture was cooled and extracted with

two 100-cc. portions of ether; the solution thus formed was shaken with three 80-cc. portions of water to remove zinc chloride, dried overnight with 5 g. of anhydrous sodium sulfate and fractionated. ^a *o*-Toluidine and *o*-ethylaniline were identified by the preparation of acetyl derivatives. ^c It is interesting to note that the ethyl ester of an alkyl substituted acetic acid can be prepared in one step from the diethyl ester of an alkyl substituted malonic acid. ⁱ The residue in the reaction flask was dark colored and tarry; possibly this was formed from the fragments of the benzyl groups by the zinc chloride. ^k The reaction mixture was cooled and extracted with two 75-cc. portions of ether. The ether solution was shaken with six 30-cc. portions of water to remove zinc chloride and dried with 5 g. of anhydrous sodium sulfate. The solvent was subsequently removed by distillation on a water-bath. Evidently the presence of the nitro group in this ester makes it more stable than ethyl benzoate.

Formic, Acetic, Propionic and *n*-Butyric Acids.—No evidence of decomposition was found in experiments with these compounds.

Benzoic, Salicylic and Cinnamic Acids.—From one-fourth mole of benzoic acid which had been refluxed with anhydrous zinc chloride for half an hour we obtained five-hundredths mole (20%) of benzene^b and carbon dioxide. A mixture containing one-fourth mole of salicylic acid was refluxed for one and one-half hours and distilled. Thirteen-hundredths mole (52%) of phenol^b and carbon dioxide were obtained. One-fourth mole of cinnamic acid was refluxed with anhydrous zinc chloride for an hour. The products were five-hundredths mole (20%) of styrene, six-hundredths mole (48%) of distyrene, carbon dioxide and 6 g. of a dark brown material which had the properties of metastyrene. The styrene and distyrene were identified by the procedures cited in a previous paper.¹

Anhydrous zinc chloride acts partly as a catalyst and partly as a reagent in some of the decompositions described in this paper.

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Summary

This paper describes the decompositions of a series of esters and acids by anhydrous zinc chloride; the transformations observed involve the elimination of an aliphatic unsaturated hydrocarbon or carbon dioxide or both. Alkyl chlorides, apparently formed by the reaction of zinc chloride with the ester, are found in the products obtained from two of the compounds studied. Several aliphatic acids remain unchanged when heated with anhydrous zinc chloride.

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