[Contribution No. 57 from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology]

CATALYSIS IN ORGANIC CHEMISTRY. III. DECOMPOSITIONS OF ESTERS BY ANHYDROUS ZINC CHLORIDE

By H. W. Underwood, Jr., and O. L. Baril

Received August 15, 1929 Published January 8, 1930

During the course of investigations of the reactions of ethers with acid chlorides[1] it was noted that aliphatic ethers yield alcohols and unsaturated hydrocarbons when heated with anhydrous zinc chloride and that diethyl phthalate is converted into phthalic anhydride. These transformations involve the splitting of the bond between the oxygen atom and alkyl groups in the ethers and in the ester. In this paper we present evidence which shows that a number of esters undergo decompositions of this or similar types in the presence of anhydrous zinc chloride.

Discussion of Experiments and Interpretation of Results

All the temperatures given are uncorrected.

General Procedure.—Pure, freshly distilled esters were used in our experiments; 0.5 mole of anhydrous zinc chloride per mole of ester was employed. Unsaturated hydrocarbons formed by the decomposition of the esters were collected as dibromides by the procedure described in a previous paper.[1] Unless otherwise stated, each reaction mixture was distilled from the zinc chloride after refluxing; the distillate was then fractionated. In some experiments the residue in the reaction flask after distillation was dark colored and somewhat tarry; however, all the distillates were free from tar, and were easily separated into the components.

Ethyl Formate, Ethyl Acetate, Ethyl Propionate and Ethyl *n*-Butyrate.—No evidence of decomposition was found in experiments with these compounds. One-half mole of ethyl formate and acetate, one-third mole of the butyrate and one-fifth mole of ethyl propionate were used; in each case more than 95% of the ester was recovered; all the mixtures were heated under reflux for three hours before distillation.

Methyl and Ethyl Benzoates, Diethyl Phthalate.—From 30 g. of ethyl benzoate which had been refluxed with anhydrous zinc chloride for two hours we obtained 7.5 g. of benzoic acid,[2] 3 g. of benzene,[2] 2 g. of ethylene dibromide and carbon dioxide. Evidently zinc chloride converts some of the benzoic acid formed by the decomposition of the ester into benzene and carbon dioxide. We obtained benzene by heating some known benzoic acid with zinc chloride.

Thirty-four grams of methyl benzoate yielded 5 g. of benzoic acid,[2] 4 g. of benzene[2] and 9 g. of the unchanged ester. No evidence of the formation of an unsaturated hydrocarbon was found. Three lots (34 g. each) of methyl benzoate were heated with zinc chloride for three hours, and the vapors from the top of the condenser were passed into 10 g. of bromine; treatment of the latter in the usual way[1] gave no ethylene dibromide. In these experiments a dark tarry residue was found in the reaction flask; possibly this was formed from the fragments of the methyl groups by the zinc chloride.

---

[1] Underwood and Wakeman, This Journal, **52**, 387 (1930); Underwood and Toone, *ibid.*, **52**, 391 (1930).

[2] The tests described by Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, **1904**, Vol. I, were used for the identification of this compound.

A mixture of 44.4 g. of diethyl *o*-phthalate and 13.6 g. of anhydrous zinc chloride solidified after being heated for half an hour under reflux. Distillation of the product gave 22 g. of phthalic anhydride;[2] 2.5 g. of ethylene dibromide was also isolated.

Ethyl and Methyl Salicylates.—One-fourth mole of ethyl salicylate and one-fifth mole of the methyl ester were refluxed with anhydrous zinc chloride for one hour and one and one-half hours, respectively. The reaction mixtures were cooled and extracted several times with pure ethyl ether; the solutions thus formed were shaken with water to remove zinc chloride, dried with anhydrous sodium sulfate and fractionated. From the ethyl salicylate we obtained 4 g. of phenol,[2] 4 g. of *o*-ethylphenol,[3] 3.5 g. of the unchanged ester, 1 g. of ethylene dibromide and carbon dioxide. Apparently two types of decomposition occurred—one involved the removal of ethylene and the other the elimination of carbon dioxide from the ester group. Methyl salicylate gave 6 g. of *o*-cresol,[2] 7 g. of the unchanged ester and carbon dioxide.

***Iso*-amyl Acetate, *Iso*-amyl *n*-Butyrate, *Iso*-amyl Benzoate.**—A mixture containing 32.5 g. of *iso*-amyl acetate was refluxed for three hours and distilled. Twenty-seven grams of the ester was recovered and 1.4 g. of acetic acid[2] was isolated. The recovered *iso*-amyl acetate decolorized a small amount of dilute potassium permanganate solution and apparently contained a trace of an unsaturated compound. Decomposition of *iso*-amyl acetate takes place only to a slight extent.

After three hours' refluxing, 31.6 g. of *iso*-amyl *n*-butyrate yielded 6 g. of *n*-butyric acid,[2] 8 g. of unchanged ester, 7 g. of a liquid with the properties of the dimer of *iso*-propylethylene, 0.2 g. of *iso*propylethylene dibromide and 4 g. of a high-boiling residue (possibly a high polymer of *iso*propylethylene). These products were difficult to fractionate. Evidently anhydrous zinc chloride splits *iso*-amyl *n*-butyrate into *n*-butyric acid and *iso*propylethylene, and polymerizes some of the latter.

From 38.4 g. of *iso*-amyl benzoate which had been heated under reflux with anhydrous zinc chloride for three hours, we obtained 11 g. of benzoic acid,[2] 0.9 g. of benzene,[2] 0.5 g. of a liquid with the properties of the dimer of *iso*propylethylene, 0.8 g. of *iso*propylethylene dibromide and carbon dioxide.

Ethyl Cinnamate.—Thirty-five and two-tenths grams of ethyl cinnamate was refluxed with anhydrous zinc chloride for three-fourths of an hour. The products are 3 g. of styrene, 6.5 g. of distyrene,[4] carbon dioxide and 5 g. of a dark brown material which had the properties of metastyrene. We also obtained 0.9 g. of ethylene dibromide. Apparently zinc chloride brings about the removal of ethylene and carbon dioxide from ethyl cinnamate, and polymerizes some of the styrene which is formed.

Diethyl Oxalate and Succinate.—When heated with anhydrous zinc chloride for an hour, one-fourth mole of diethyl oxalate was transformed into a white solid which weighed 33.5 g. This material was insoluble in hot and cold water and did not melt at 360°. In order to determine whether the solid contained oxalic acid, a sample was heated for some time at 150°; no sublimation occurred. Ignition of the product caused the distillation of an organic liquid and gave a white residue which contained zinc. Another experiment with diethyl oxalate was carried out and the gases evolved during the heating were investigated. Carbon dioxide, ethyl chloride and a gas which behaved like a saturated aliphatic hydrocarbon were found; no ethylene was detected. The results of the experiments indicate that zinc chloride reacts with diethyl oxalate to give ethyl chloride and a zinc salt; some of the ester is split into carbon dioxide

---

[3] This compound was identified by the preparation of the tribromo derivative; the procedure described by Stoermer and Kahlert, *Ber.*, **35**, 1631 (1902), was used.

[4] The styrene and distyrene were identified by the preparation of the dibromides; the procedures described by Glaser, *Ann.*, **154**, 154 (1870), and by Fittig and Erdmann, *ibid.*, **216**, 190 (1882), were used.

and a saturated aliphatic hydrocarbon, possibly butane. Diethyl succinate behaved like diethyl oxalate when heated with anhydrous zinc chloride.

Diethyl Malonate.—From one-fourth mole of diethyl malonate which had been refluxed with anhydrous zinc chloride for three hours we obtained 6 g. of ethyl acetate, 6 g. of unchanged ester and carbon dioxide; 0.2 g. of ethylene dibromide was secured. In a check run we isolated 8 cc. of a liquid which had the boiling point and other properties of *n*-pentane. Evidently two types of decomposition occurred—one involved the removal of both ethylene and carbon dioxide from one of the ester groups and the other involved the elimination of carbon dioxide from each ester group.

Summary

When ethyl formate, acetate, propionate and *n*-butyrate are heated with anhydrous zinc chloride each ester remains unchanged. Under similar conditions diethyl *o*-phthalate gives phthalic anhydride and ethylene, and ethyl benzoate yields benzoic acid, benzene and ethylene. Ethyl salicylate is transformed into phenol and *o*-ethylphenol through the loss of ethylene and carbon dioxide. From methyl benzoate we obtained benzoic acid and benzene, and from methyl salicylate we secured *o*-cresol and carbon dioxide. Anhydrous zinc chloride splits *iso*-amyl acetate, *n*-butyrate and benzoate into the corresponding acids and *iso*propylethylene, and polymerizes some of the latter. Ethyl cinnamate yields styrene, distyrene, metastyrene, carbon dioxide and ethylene. Diethyl malonate gives ethyl acetate, *n*-pentane, ethylene and carbon dioxide. Anhydrous zinc chloride reacts with diethyl oxalate forming ethyl chloride and a zinc salt; some of the ester is decomposed into carbon dioxide and a saturated aliphatic hydrocarbon. Diethyl succinate behaves like diethyl oxalate.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

SKRAUP'S REACTION APPLIED TO THE PHENYLENEDIAMINES. PREPARATION OF THE PHENANTHROLINES AND RELATED DIPYRIDYLS

BY C. R. SMITH

RECEIVED AUGUST 16, 1929 PUBLISHED JANUARY 8, 1930

The Skraup reaction as applied to monoamines has proved to be a valuable synthetic method, but the double Skraup reaction, either in the original or in a modified form, applied to diamines, has generally given unsatisfactory results, especially with *p*- or *m*-phenylenediamine. It seems that either no attempts have been made to apply the reaction to *o*-phenylenediamine or, more probably, that no pure compounds were isolated from the resulting products and hence the results were not reported.

The writer has studied the production of phenanthrolines from the phenylenediamines and has found that results which compare favorably with the average monoamine as to yield and ease of purification can be