chloride; ketones are formed by the introduction of an acetyl or benzoyl group into the aromatic nucleus.

Acetic, chloro-acetic, propionic, *n*-butyric, *iso*valeric, oxalic, malonic, succinic, benzoic, phenylacetic, hydrocinnamic, *p*-toluic, mandelic, anisic, *p*-chlorobenzoic, *o*-, *m*- and *p*-nitrobenzoic, 3,5-dinitrobenzoic, *p*-aminobenzoic, *o*-phthalic and diphenic acids and the anhydrides of acetic, propionic, *n*-butyric, *iso*valeric, succinic, benzoic, *o*-phthalic and diphenic acids are converted into ethyl esters by treatment with anhydrous ethyl ether containing dry hydrogen bromide. Stearic, picric, *p*-toluenesulfonic and 2,4,-6-trinitrobenzoic acids do not react with ethyl ether in the presence of hydrogen bromide.

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CATALYSIS IN ORGANIC CHEMISTRY. II. MECHANISM OF THE REACTIONS OF ETHERS WITH ACID CHLORIDES, ACIDS AND ANHYDRIDES

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In a previous paper[1] it was pointed out that a number of acid chlorides, acids and anhydrides are converted into esters by treatment with aliphatic ethers in the presence of anhydrous zinc chloride or hydrogen bromide. Zinc chloride might increase the reactivity of aliphatic ethers by loosening the alkyl groups so that a metathesis of the type $RCOCl + R'OR' = RCOOR' + R'Cl$ would occur. The possibility that aliphatic ethers may be split into two or more compounds capable of independent existence also deserves consideration. Experiments described in this paper show that ethyl, *iso*propyl, *n*-butyl and *iso*-amyl ethers yield small amounts of the corresponding alcohols and unsaturated hydrocarbons when heated with anhydrous zinc chloride. When an alcohol thus formed is esterified by an acid chloride, splitting of the ether continues, and the hydrogen chloride produced may convert some of the alcohol into an alkyl chloride. Equations for the transformations of acetyl chloride and ethyl ether might be written as follows

$$CH_3CH_2OCH_2CH_3 = CH_3CH_2OH + CH_2{=}CH_2$$
$$CH_3CH_2OH + CH_3COCl = CH_3COOCH_2CH_3 + HCl$$
$$CH_3CH_2OH + HCl = CH_3CH_2Cl + H_2O$$

The reaction of ethyl ether with acetyl chloride takes place in the presence of a very small amount of anhydrous zinc chloride, and the latter can be used several times; apparently zinc chloride acts as a true catalyst.

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[1] Underwood and Wakeman, THIS JOURNAL, **52**, 387 (1930).

We have also shown that ethyl, *iso*propyl, *n*-butyl and *iso*-amyl ethers are converted into alkyl bromides and alcohols when treated with dry hydrogen bromide.

Discussion of Experiments and Interpretation of Results

All the temperatures given are uncorrected.

Purification of Ethers.—Ethyl ether was purified by the method cited in a previous paper.[1] An explosion occurred during the distillation of *iso*propyl ether which had been purchased as pure; tests showed that this ether contained peroxides. The procedure described below was employed for the purification of *iso*propyl, *n*-butyl and *iso*-amyl ethers. In order to remove peroxides each compound was washed with one-fifth its volume of 10% potassium iodide solution as often as necessary (one to ten times); the iodine produced in this treatment was removed by shaking the ether with one-fifth its volume of 10% sodium thiosulfate solution. Next the compound was washed with one-fifth its volume of water, then cooled in ice, shaken with one-fourth its volume of a mixture of sulfuric acid and water (equal volumes of each) and finally washed with water. After being dried with anhydrous sodium sulfate the ether was distilled. The boiling points of the purified ethers were as follows: ethyl, 34–34.5°; *iso*propyl, 68–68.5°; *n*-butyl, 139.5–140.5°; *iso*-amyl, 169–170°.

Ethers and Anhydrous Zinc Chloride.—Ethyl, *iso*propyl, *n*-butyl and *iso*-amyl ethers were refluxed for two hours with anhydrous zinc chloride; one half mole of the latter per mole of ether was used. In each experiment the top of the reflux water condenser was connected with two flasks; one of these contained 10 g. of bromine to absorb unsaturated hydrocarbons, and the other flask was a trap. The quantities of ethers used are as follows: ethyl, 44.4 g.; *iso*propyl, 12.3 g.; *n*-butyl, 26 g.; *iso*-amyl, 31.6 g. *n*-Butyl ether yielded 0.5 cc. of a liquid boiling at 70–130°; a drop of this distillate gave the odor of *n*-butyl acetate when mixed with a drop of acetyl chloride. The remainder of the liquid boiling at 70–130° was added to 0.1 g. of 3,5-dinitrobenzoyl chloride; the mixture was allowed to stand for five minutes, placed in hot water for two minutes and filtered. The solid left on the filter was added to 5 cc. of 3 *N* sodium carbonate solution and well stirred in order to remove excess dinitrobenzoyl chloride. The insoluble residue was filtered and washed with 5 cc. of 3 *N* sodium carbonate solution and 5 cc. of water. After three crystallizations from alcohol the solid melted at 63–64°; this is the melting point of *n*-butyl 3,5-dinitrobenzoate.[2] A parallel experiment with some *n*-butyl ether which had not been treated with zinc chloride gave no ester. *Iso*-amyl ether yielded 0.6 cc. of a liquid boiling at 70–165°. By use of the procedure described above, 0.1 g. of *iso*-amyl 3,5-dinitrobenzoate (m. p. 60–61°) was isolated. A parallel experiment with *iso*-amyl ether which had not been heated with zinc chloride gave no ester.

The bromine used to absorb unsaturated hydrocarbons which might be formed in the splitting of the ethers was treated with 10% sodium thiosulfate solution to remove unchanged bromine and the resulting mixture was extracted with 40 cc. of pure ethyl ether. The ether layer was dried with anhydrous sodium sulfate and distilled. No dibromides were isolated in any of our preliminary experiments; probably the amounts of unsaturated hydrocarbons formed were too small to be detected by this method. However, it was found that the ethers apparently contained traces of unsaturated compounds after heating with zinc chloride, since small portions of the ethers decolorized very dilute potassium permanganate solution.

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[2] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, **1904**, Vol. I, p. 168.

In preliminary experiments with ethyl and *iso*propyl ethers we were unable to prepare dinitrobenzoates from the distillates. However, four drops of the distillate from *iso*propyl ether gave the iodoform reaction. Three and one-half moles of each ether was refluxed for three hours with zinc chloride and distilled. No portions of the distillates boiled as high as the corresponding alcohols, but dinitrobenzoates were obtained from the first 8 cc. of each distillate; these fractions also gave the iodoform test, and enough of the latter for a melting point was secured. Parallel experiments with ethers which had not been heated with zinc chloride gave negative results.

It was necessary to use 500 g. of the ethers in order to isolate the dibromides of the unsaturated hydrocarbons formed in the splittings by zinc chloride; very small amounts of these dibromides were obtained.

Anisole, phenetole and diphenyl ether (0.1 mole of each) were heated under reflux for two hours with anhydrous zinc chloride (0.05 mole). Upon distillation of each mixture the ether was recovered practically quantitatively; all of the liquid boiled within one degree. The distillates gave no color test for phenol when treated with ferric chloride solution; a violet color was readily obtained by adding one drop of dilute phenol solution and one of ferric chloride solution to a portion of each distillate. Evidently the carbon–oxygen bonds in these aromatic ethers are not broken by anhydrous zinc chloride under the conditions tried.

Ethers and Acid Chlorides.—The experiments described below were carried out to secure information about the products other than esters which are formed in the reactions of aliphatic ethers with acid chlorides. In each run 0.4 mole of zinc chloride per mole of acid chloride was used. Fifty-two and three-tenths grams of acetyl chloride and 54.2 g. of ethyl ether gave 37.8 and 30.2% yields of ethyl acetate and ethyl chloride and a trace of ethylene dibromide; 20.4 g. of *iso*propyl ether and 19.6 g. of acetyl chloride gave 66.5 and 30.6% yields of *iso*propyl acetate and *iso*propyl chloride and 1.8 g. of propylene dibromide. By distillation of the reaction mixture from 50 g. of *n*-butyl ether and 27.5 g. of acetyl chloride we obtained 65.7 and 29.9% yields of *n*-butyl acetate and *n*-butyl chloride and 10.6% of butylene dibromide. One-tenth mole of acetyl chloride and 0.11 mole of *iso*-amyl ether gave 12 and 6% yields of *iso*-amyl acetate and *iso*-amyl chloride, and 0.1 g. of *iso*propylethylene dibromide.

Catalytic Action of Anhydrous Zinc Chloride.—A mixture of 31.4 g. of acetyl chloride and 32.6 g. of pure anhydrous ethyl ether was heated under reflux for three hours with 5.44 g. of anhydrous zinc chloride, and then distilled from the latter through a long fractionating column. The yield of ethyl acetate was 77%. (This result shows that some ethyl acetate is lost in the isolation procedure, involving extractions with ether and washing the ether solution, described in a preceding paper[1] and followed in previous experiments.) The zinc chloride was used for three more runs; the yields of ethyl acetate were 78, 77 and 79%. Evidently zinc chloride acts as a true catalyst in this reaction.

Ethers and Hydrogen Bromide.—Hydrogen bromide was prepared and dried by the procedure described in a previous paper.[1] In experiments with *n*-butyl ether (22.1 g.), *n*-butyl ether (22.1 g.) + glacial acetic acid (10.2 g.), and *n*-butyl ether (22.1 g.) + acetic anhydride (17.3 g.) hydrogen bromide was passed into the liquids for six hours, with cooling during the last two hours; 0.36 mole of hydrogen bromide was absorbed in each case. Dry hydrogen bromide was passed into 20.4 g. of glacial acetic acid until 0.143 mole had been absorbed; this required two hours. The flasks containing these mixtures were closed with tight-fitting stoppers held in place by wire and covered with collodion. After standing for ten days at room temperature, the liquids were refluxed for three and one-half hours in a water-bath, and the layers which had formed were separated. In each case the non-aqueous layer was washed with dilute sodium carbonate solution and with water, dried with anhydrous sodium sulfate and distilled through a long fractionating column. The *n*-butyl ether yielded 29.2 g. of *n*-butyl bromide. The *n*-butyl ether–acetic acid mixture gave 20.4 g. of *n*-butyl bromide, 1 g. of *n*-butyl acetate and 9.5 g. of acetic acid. From the acetic anhydride–ether mixture we obtained 16.3 g. of *n*-butyl bromide, 2 g. of *n*-butyl acetate and 8 g. of impure acetic acid. After standing for ten days, mixtures of 20.4 g. of acetic acid + 0.143 mole of hydrogen bromide, and 17.3 g. of acetic anhydride + 0.2 mole of hydrogen bromide were distilled through a long fractionating column; the former gave 17 g. of acetic acid and the latter yielded 2 g. of acetyl bromide and 9 g. of acetic acid. These experiments show that acetic anhydride is converted into acetyl bromide and acetic acid by reaction with hydrogen bromide.

In order to determine the behavior of *n*-butyl ether when treated with less hydrogen bromide than was used in previous experiments, hydrogen bromide was passed into 19.7 g. of the ether (0.15 mole) until 0.25 mole had been absorbed. After the mixture had stood for sixteen hours, it was heated under reflux for three hours. The two layers which formed were separated, washed with dilute sodium carbonate solution, dried with anhydrous sodium sulfate and distilled through a long fractionating column. Nineteen grams of *n*-butyl bromide and 1.5 g. of *n*-butyl alcohol were obtained; the latter was identified by preparation of the 3,5-dinitrobenzoate. Similar experiments with ethyl, *iso*propyl and *iso*-amyl ethers gave the alkyl bromide and a small amount of the corresponding alcohol in each case. By use of an excess of hydrogen bromide ethyl ether was entirely converted into ethyl bromide.

Summary

When heated with anhydrous zinc chloride ethyl, *iso*propyl, *n*-butyl and *iso*-amyl ethers yield small amounts of the corresponding alcohols and unsaturated hydrocarbons. When an alcohol thus formed is esterified by an acid chloride, splitting of the ether continues, and the hydrogen chloride produced in the esterification converts some of the alcohol into an alkyl chloride. Under the conditions tried the carbon–oxygen bonds in anisole, phenetole and diphenyl ether are not broken by zinc chloride. The reaction of ethyl ether with acetyl chloride takes place in the presence of a very small amount of anhydrous zinc chloride, and the latter can be used several times; apparently zinc chloride acts as a true catalyst.

Ethyl, *iso*propyl, *n*-butyl and *iso*-amyl ethers are converted into alcohols and alkyl bromides by treatment with dry hydrogen bromide. The reaction of acetic anhydride with anhydrous hydrogen bromide gives acetyl bromide and acetic acid.

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