

$\beta',\beta'$ -dinitropyrocoll. This latter is only sparingly soluble in hot glacial acetic acid and when so dissolved may be crystallized out in fine, yellow prisms. It is best however to crystallize it from nitrobenzene, in which it is more soluble.  $\beta',\beta'$ -Dinitropyrocoll is fairly soluble in nitrobenzene or acetone; slightly soluble in acetic acid, alcohol, benzene, or ethyl acetate, and practically insoluble in ether, ligroin, chloroform or water. It decomposes without melting at  $315-20^\circ$ . Upon hydrolysis with strong alkali, in the same manner as directed for the preceding dinitropyrocolls, this product yielded  $\beta'$ -nitro- $\alpha$ -carbopyrrolic acid, melting at  $217^\circ$ . And again by the action of acetic anhydride this latter is most readily converted into the original  $\beta',\beta'$ -dinitropyrocoll.

0.1392 g. subst. gave 0.2211 g.  $\text{CO}_2$  and 0.0225 g.  $\text{H}_2\text{O}$ ; 0.1734 g. subst. gave 32.8 cc.  $\text{N}_2$  ( $25.5^\circ$  and 741.3 mm. over  $\text{H}_2\text{O}$ ).

Calc. for  $\text{C}_{10}\text{H}_4\text{O}_6\text{N}_4$ : C, 43.46; H, 1.46; N, 20.30. Found: C, 43.33; H, 1.81; N, 20.42.

Since  $\beta'$ -nitro- $\alpha$ -carbopyrrolic acid is that particular acid which is easily synthesized from glycine ester and nitromalonic aldehyde,<sup>1</sup> its preparation by the nitration of pyrocoll is not to be advised. Furthermore, the nitration of pyrocoll with this acid in view has never yielded more than 10% of the theoretical quantity. It should be stated further that a small amount of this  $\beta',\beta'$ -dinitropyrocoll is also usually found in the product obtained from the nitration of pyrocoll according to the method of Ciamician and Danesi. In this connection we wish to express our indebtedness to Mr. E. M. Honan, of this laboratory, for the care he has taken in checking our results.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF VANDERBILT UNIVERSITY.]

## THE REACTION BETWEEN ALCOHOLS AND AQUEOUS SOLUTIONS OF HYDROCHLORIC AND HYDROBROMIC ACIDS.

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In a previous paper<sup>2</sup> it was shown that a large number of aliphatic and aromatic alcohols react with aqueous solutions of hydrobromic acid and hydriodic acid and form the corresponding organic bromides and iodides, and that, in certain cases, analogous reactions take place with hydrochloric acid. When the alcohols and the constant-boiling mixtures of the acids and water were distilled, good yields of the halides were obtained. The substances formed in this way were free from the impurities which are present when phosphorous compounds are used to prepare them. The method has been used when especially pure halides

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Am. Chem. J.*, 38, 627 (1907).

have been required for investigation,<sup>1</sup> and it has found its way into laboratory guides.<sup>2</sup> On account of the fact that the method has proved to be a valuable one in certain cases, it seemed advisable to study the behavior of a greater variety of alcohols with aqueous solutions of hydrochloric acid and hydrobromic acid. Up to the present no work, in addition to that already published, has been done with hydriodic acid, since in all the cases studied it was found that hydriodic acid behaved in the same way as hydrobromic acid; the only difference observed was that slightly better yields were obtained with the former acid. Alcohols were selected for study to throw light on the following points: the effect of structure on the readiness with which the reaction takes place, the cause of the difference between the behavior of hydrochloric acid and that of hydrobromic acid, the value of hydrobromic acid as a reagent to test for an alcoholic hydroxyl group, and, finally, the applicability of the reaction as a general preparative method for alkyl halides.

The effect of the structure of the alcohol on its reactivity is marked. The rate at which primary alcohols react with aqueous hydrobromic acid (sp. gr. 1.49) decreases, in general, with increase in molecular weight. The alcohol with the highest molecular weight studied was cetyl alcohol; a yield of 72% of bromide was obtained after heating for four hours a mixture of the alcohol and acid in the molecular proportion of one of the former to four of the latter.

The conclusion drawn from the previous work on primary, secondary, and tertiary alcohols, namely, that the ease of reaction increases in the above order, was confirmed.

A study of the difference between the behavior of hydrochloric acid and hydrobromic acid brought out some interesting results, which will be the subject of further study, since no satisfactory reason is yet evident for the great difference in the behavior of these two acids. It was shown in the previous paper that benzyl alcohol reacted readily with aqueous hydrochloric acid, whereas ethyl alcohol did not. The replacement of the methyl radical by phenyl brought about this difference. A study of a number of primary saturated aliphatic alcohols has been made; none reacts with aqueous hydrochloric acid when heated in an open vessel. The influence of the presence of a phenyl radical in an alcohol is marked. To determine the effect of the position of this radical on the behavior of the alcohol with hydrochloric acid, alcohols of the following structures were

<sup>1</sup> See Michael, *Ann.*, **379**, 291 (1911) and **393**, 95 (1912). Michael found that in the case of some of the higher alcohols the bromides prepared by him from alcohols and aqueous hydrobromic acid contained small quantities of unsaturated hydrocarbons; the latter were removed by shaking the halide with a dilute solution of potassium permanganate. In order to avoid the formation of by-products, the reaction should be carried out at as low a temperature as possible.

<sup>2</sup> See "Practical Organic Chemistry," Sudborough and James; Van Nostrand.

studied under the same conditions:  $C_6H_5CH_2OH$ ,  $C_6H_5CH_2CH_2OH$ , and  $C_6H_5CH_2CH_2CH_2OH$ . Benzyl alcohol was readily converted into benzyl chloride in the cold by concentrated hydrochloric acid, and when distilled with acid of the specific gravity 1.1 gave a good yield of the chloride. Primary phenylethyl alcohol gave but a trace of the chloride, and there was no reaction with the derivative of propyl alcohol.

Since the phenyl radical is negative, it seemed possible that an aliphatic radical more negative than methyl or ethyl if joined to the carbinol carbon, might produce an effect similar to that of the aryl radical. Accordingly, the behavior of allyl alcohol,  $CH_2 = CH.CH_2OH$ , with hydrochloric acid (sp. gr. 1.1) was studied. In this case the vinyl radical, which has a negative nature due to the double bond, replaces the phenyl radical of benzyl alcohol. When allyl alcohol was distilled with a large excess of the constant-boiling mixture of hydrochloric acid and water, a yield of .50% of allyl chloride was obtained. It is interesting to note in this connection that the ionization constant of benzoic acid,  $C_6H_5.COOH$ , is 0.0060, and that of acrylic acid,  $CH_2 = CH.COOH$ , is 0.0056. The phenyl radical and the vinyl radical have approximately the same effect on the ionization of the acids made up of these radicals and the carboxyl group; they have thus approximately the same electronegative character. It is probable that this character is a determining factor in the behavior of compounds containing these groups; the similarity of the reactivity of benzyl alcohol and allyl alcohol is an example. The behavior of other substances which contain the vinyl radical resembles markedly that of compounds of analogous structure containing the phenyl radical. This important fact is being investigated further.

As has been stated above, there was no chloride formed from primary phenylpropyl alcohol,  $C_6H_5CH_2CH_2CH_2OH$ , and hydrochloric acid; cinnamyl alcohol,  $C_6H_5CH = CHCH_2OH$ , on the other hand, gave a yield of 80% of the chloride when distilled with aqueous hydrochloric acid (sp. gr. 1.1). The results with the aromatic alcohols and with the two unsaturated alcohols bring out the important fact that the reactivity of alcohols with hydrochloric acid is facilitated by the accumulation of negative radicals around the carbinol carbon atom. If the reaction between an alcohol and an acid is similar to that between a base and an acid, it appears that the accumulation of negative radicals increases basicity. This point of view, which seems far from reasonable at first sight, is not necessarily false. It is possible that the proper balance of the so-called negative radicals may produce the behavior which we associate with positive radicals. The case of the iodonium compounds is an example; by the union of two negative phenyl radicals with an iodine atom, we obtain a group  $(C_6H_5)_2I$ , which has marked basic properties, since diphenyliodonium hydroxide  $(C_6H_5)_2I.OH$ , is a comparatively strong base.

Recent work on the base-forming property of oxygen brings out the fact that when radicals containing double bonds are linked to oxygen the resulting compounds show a greater basicity than those containing saturated radicals. Since radicals containing double bonds are more negative than the corresponding saturated ones, the results indicate that increase to a certain degree in the negativity of the substituents in a molecule increases the basicity or positive character of the group made up of these radicals. Experiments which have been carried out to test this view indicate that the basicity of alcohols can be increased by grouping negative radicals around the carbinol carbon atom.

It is possible that the reaction between an alcohol and an acid is not of the same nature as that between an inorganic base and an acid. Experiments are now in progress to bring additional light on this important question. It is highly probable that other factors than those of positivity and negativity are of importance in the reactions studied. The experiments in progress include a search for these factors.

In order to study further the effect of the nature of the radicals present in an alcohol on its reactivity with hydrochloric acid, the three nitrobenzyl alcohols were investigated. In no case was the hydroxyl group replaced by chlorine. The introduction of the nitro group into the phenyl radical markedly increases its negativity, since the ionization constants of the nitrobenzoic acids are much greater than that of benzoic acid. It is evident, therefore, that if the negativity of a group is a factor in determining the basicity of an alcohol, there are limits in the negativity, between which the highest degree of basicity is produced. The effect of the nature of radicals on basicity is being studied from this point of view.

It was stated above that increase in molecular weight in the paraffin series decreases the activity of the alcohol and that secondary alcohols react more readily than primary alcohols. Secondary butyl alcohol formed a chloride with hydrochloric acid, but secondary octyl alcohol did not. The effect of increased molecular weight in this case overcame the effect of the secondary structure.

All the alcohols studied formed bromides when heated with the constant-boiling mixture of hydrobromic acid and water. Since 27 aliphatic and aromatic alcohols, which vary markedly in structure, have been studied, it seems that the reaction can be advantageously used as a reliable qualitative test for an alcoholic hydroxyl group in monatomic alcohols. Aqueous hydriodic acid reacts with certain esters and ethers, and, as a consequence, cannot be used in testing for the presence of alcoholic hydroxyl. It seemed desirable, therefore, to determine if aqueous hydrobromic acid reacted in an analogous way. The acid did not convert ether or ethyl acetate into ethyl bromide when the substances were distilled together. It is probable, therefore, that ethers and esters which

behave normally will not react with hydrobromic acid under the conditions to be used in the test for the hydroxyl group, namely, heating the substance to be investigated in an open vessel with the constant-boiling aqueous solution of hydrobromic acid. It is probable that in certain cases hydrobromic acid is a better reagent for alcoholic hydroxyl than acetyl chloride, or acetic anhydride, since these substances react at times with acidic hydroxyl.

The statements above refer to monatomic alcohols. A study has been begun of the behavior of polyatomic alcohols with hydrobromic acid. Glycol was in part converted into ethylene bromide, and glycerol into a bromohydrin. The yields in both cases were small. Details of the reactions are given in the experimental part of the paper.

Since in all the cases of monatomic alcohols studied good yields of bromides and iodides were obtained, the reactions can be advantageously used to prepare these compounds. In this paper no work on hydriodic acid is reported, but as has been stated, the reactions with this acid take place more readily than with hydrobromic acid, and it is highly probable that iodides could be prepared from the alcohols whose behavior with hydrobromic acid is described below.

#### Experimental Part.<sup>1</sup>

In the paper to which reference has been made a description was given of the action of hydrochloric, hydrobromic and hydriodic acids on the alcohols containing the following radicals: methyl, ethyl, propyl, isopropyl, isobutyl, secondary butyl, tertiary butyl, isoamyl, allyl, benzyl, diphenylmethyl, triphenylmethyl and tritolylmethyl. In this paper are given the results of the study of the alcohols containing the following radicals: allyl, tertiary amyl, heptyl (pentamethylethanol), normal octyl, secondary octyl, cetyl, ortho-, meta-, and paranitrobenzyl, primary phenylethyl, primary phenylpropyl and cinnamyl. Glycol and glycerol were also studied.

**Allyl Alcohol.**—The alcohol was mixed with varying quantities of hydrochloric acid and slowly distilled. The highest yields of chloride were obtained when the constant-boiling mixture of the acid and water was used. With concentrated hydrochloric acid a higher percentage of alcohol distilled over unchanged than when the solution of acid containing 20.2% hydrogen chloride was used. A series of experiments showed that the highest yield was obtained when 1 g. molecule of the alcohol was distilled with 5 g. molecules of the constant-boiling mixture of hydrogen chloride and water. Under these conditions 10 g. of allyl alcohol and 160 g. of hydrochloric acid (sp. gr. 1.1), gave 7 g. of allyl chloride. After drying and distillation the yield was 50% of the theoretical. The yields were practically the same when 10 and 20 g. molecules of acid were used.

<sup>1</sup> The work described was done in the laboratory of Simmons College.

The yields of allyl bromide (61%) and allyl iodide (58%), reported in the previous paper were obtained with the commercial alcohol. When the pure alcohol was used under the same conditions, 1 molecule of alcohol to 3 molecules of the constant-boiling acids, the yield of bromide was found to be practically the theoretical; the yield of iodide was 84%.

**Tertiary Amyl Alcohol.**—When 5 g. of the alcohol were distilled with 29 g. of hydrobromic acid (sp. gr. 1.49) (molecular ratio 1 : 3), the yield of tertiary amyl bromide was 95% of the theoretical. When the constant-boiling mixture of hydrochloric acid and water was used in the same molecular ratio, the yield of chloride was 93%; under the same conditions with concentrated hydrochloric acid the yield was 98% of the theoretical.

**Normal Octyl Alcohol.**—With increasing molecular weight the reaction between the alcohols and hydrobromic acid took place more slowly. In order to increase the yield of halide the alcohol was accordingly boiled with the acid in a flask provided with a reflux condenser. A large excess of acid was required to produce satisfactory yields. When 5 g. of normal octyl alcohol were heated for one hour with 25.5 g. of hydrobromic acid (four times the theory), 3.5 g. of the bromide were obtained. When the same molecular proportions were used and the mixture heated two hours, 10 g. of the alcohol gave 10 g. of bromide, which is 66% of the theoretical. The alcohol which distilled unchanged with the bromide was removed by shaking the mixture with ice-cold concentrated sulfuric acid. The bromide was then washed with water, dried over calcium chloride and distilled. The bromide boiled at 201–202° (corrected).

**Secondary Octyl Alcohol.**—Ten grams of the alcohol were heated for 2 hours with 51 g. of hydrobromic acid (molecular ratio 1 : 4). The bromide was purified as described above. The yield of bromide boiling at 188–189° (corrected), was 60% of the theoretical.

When the alcohol was boiled with hydrochloric acid only a trace of chloride was formed.

**Pentamethylethanol,**  $(\text{CH}_3)_3\text{C}.\text{C}(\text{CH}_3)_2.\text{OH}$ .—Since tertiary butyl alcohol reacts much more readily with acid than normal butyl alcohol, the compound of the structure given above was prepared and studied. It has the tertiary structure and, in addition, a tertiary butyl radical. It was thought that the alcohol might show more base-like properties than any alcohol yet investigated. The compound was prepared from pinacoline and methyl iodide by the method described by Henry.<sup>1</sup> The yields in two preparations were 68% and 75%. The alcohol was converted in the cold by hydrobromic acid into the bromide. The reaction took place slowly, since both the alcohol and bromide are insoluble in the acid. It was found difficult to separate the alcohol from the bromide, as both

<sup>1</sup> *Rec. trav. chim.*, 26, 84 and 106 (1907).

sublime at low temperatures. The extent to which the reaction took place between the alcohol and acid was determined by titrating the acid which was left over after reaction had taken place. Since the basicity of this alcohol appeared to be greater than that of any of the others studied, the extent to which reaction took place between equal molecular quantities of the alcohol and hydrobromic acid diluted with water was investigated. The constant-boiling mixture of hydrobromic acid and water contains its constituents approximately in the ratio of 1 of the acid to 5 of water. When pentamethylethanol, hydrogen bromide, and water in the molecular ratio 1 : 1 : 7.5, respectively, were allowed to react at room temperature, 16% of the alcohol was converted into bromide; when the mixture was heated at 60° for ten minutes the percentage of bromide formed was increased to 25. When tertiary butyl alcohol was studied under the same conditions the results were approximately the same. Since the alcohol did not possess basic properties markedly greater than those of tertiary butyl alcohol, it was not investigated further.

**Cetyl Alcohol.**—Ten grams of the alcohol were heated with 33 g. of constant-boiling hydrobromic acid (molecular ratio 1 : 5) for four hours. The product was separated and extracted with hot alcohol, which dissolved out the alcohol which had not reacted. The weight of the bromide formed was 9.5 g., which is 80% of the theoretical.

***o*-Nitrobenzyl Alcohol.**—Hydrochloric acid did not convert the alcohol into the chloride. When 1 g. of the alcohol was slowly heated in a water bath with 3.3 g. of hydrobromic acid (sp. gr. 1.49), the alcohol dissolved when the temperature was 50°. At 75° the solution clouded and the bromide separated slowly. After heating 1.5 hours, the product was separated, washed with concentrated hydrochloric acid to remove any unchanged alcohol. The bromide obtained melted at about 39°; after recrystallization from a mixture of alcohol and water the melting point was 46–47°. The yield of pure bromide was 85% of the theoretical. An analysis for halogen gave 36.79% bromine; the theoretical is 37.03%.

***m*-Nitrobenzyl Alcohol.**—The alcohol was not converted into the chloride by hydrochloric acid. When 1 g. of the alcohol was heated on a water bath with 3.3 g. of hydrobromic acid the bromide began to separate at 83°; after heating for 1.5 hours the bromide was separated and weighed. The yield was 64% of the theoretical. The bromide melted at 58–59°, which is the recorded melting point.

***p*-Nitrobenzyl Alcohol.**—The alcohol was not converted into the chloride when heated with hydrochloric acid. When 1 g. of the alcohol was heated with 3.3 g. of hydrobromic acid the bromide began to separate at about 85°. After heating 1.5 hours the product was separated, washed with concentrated hydrochloric acid, and dried. The yield of bromide, which melted at 99–100°, was 1.4 g., 99% of the theoretical.

**Primary Phenylethyl Alcohol**,  $C_6H_5CH_2CH_2OH$ .—Ten grams of the alcohol were heated with 75 g. of hydrochloric acid (sp. gr. 1.1) (molecular ratio 1 : 5) for 2 hours. The product was separated and distilled. A very small amount of the chloride was obtained. Five grams of the alcohol were slowly distilled with 28 g. of hydrobromic acid (molecular ratio 1 : 4). The product was washed with hydrochloric acid, dried, and distilled. The bromide boiled at  $108-112^\circ$  at 17 mm. pressure. The yield was 86% of the theoretical.

**Secondary Phenylethyl Alcohol**,  $C_6H_5CH_2CHOH$ .—Five grams of the alcohol were distilled with 74 g. of constant-boiling hydrochloric acid (molecular ratio 1 : 10). The product was separated, dried and distilled. It was evident from the irregular boiling point of the chloride that a secondary reaction had taken place. It is probable that as a result of the long heating an unsaturated hydrocarbon had been formed in appreciable quantities. To avoid this the alcohol was shaken at room temperature with the acid. Ten grams of the alcohol and 75 g. of hydrochloric acid (sp. gr. 1.1) were shaken vigorously for about ten minutes. The product was separated, dried, and distilled under diminished pressure. Eight grams of the chloride, which boiled at  $90-91^\circ$  at 33 mm. pressure, were obtained. The yield of pure chloride was about 75% of the theoretical. Five grams of the alcohol were distilled with 28 g. of the constant-boiling hydrobromic acid (molecular ratio 1 : 4). The bromide obtained distilled at  $106^\circ$  at 31 mm. pressure. The yield was 95% of the theoretical.

**Primary Phenylpropyl Alcohol**,  $C_6H_5CH_2CH_2CH_2OH$ .—When the alcohol was boiled with hydrochloric acid a product which did not boil constantly was obtained. It is probable that the mixture contained an unsaturated hydrocarbon. No chloride was isolated. Ten grams of the alcohol were heated for two hours with 22 g. of hydrobromic acid (molecular ratio 1 : 2). The product, after washing and drying, was distilled under diminished pressure. Eight grams of bromide were obtained, which boiled at  $128-129^\circ$  (corrected) at 29 mm. The yield was 63% of the theoretical.

**Cinnamyl Alcohol**.—Five grams of the alcohol were distilled with 33.5 g. of constant-boiling hydrochloric acid (molecular ratio 1 : 5). The product was solidified by cooling, filtered, and washed. It was then melted and filtered twice through dry filter paper. A clear oil was obtained which melted at  $4-9^\circ$ . The recorded melting point was  $8-9^\circ$ . It contained 23.37% chlorine; the theoretical is 23.27%. The yield of chloride was 79% of the theoretical.

Five grams of the alcohol were distilled with 19.5 g. of hydrobromic acid (molecular ratio 1 : 3). The product was treated in the manner used to purify the chloride. It melted at  $18-23^\circ$ , and decomposed when boiled.

The yield was 93% of the theoretical. The percentage of bromine formed was 40.14; the theoretical percentage is 40.61.

**Glycol.**—Ten grams of the alcohol were heated 2 hours with 145 g. of constant-boiling hydrochloric acid (molecular ratio 1 : 5). The mixture was then fractionated; neither ethylene chloride nor the chlorohydrin were obtained. Twenty grams of glycol were boiled for 2 hours with 165 g. of hydrobromic acid (molecular ratio 1 : 3). The mixture was then fractionated, using a Glinsky tube. No bromohydrin was obtained, but there were formed 8 cc. of an insoluble oil which proved to be ethylene bromide, the yield being 36% of the theoretical. In another experiment when the mixture was heated for a shorter time, some of the bromohydrin was obtained. The exact conditions which determine replacement of one and two hydroxyl groups by bromine were not determined.

**Glycerol.**—A mixture of 10 g. of glycerol and 55 g. of hydrobromic acid (molecular ratio 1 : 3) was distilled slowly at ordinary pressure until the temperature of the vapor was 140°. The distillation was continued at 33 mm. pressure. The product obtained boiled at 146–175°. After three fractionations at 30 mm. pressure 6 g. of an oil which boiled at 145–147° (corrected) were obtained. The bromohydrins have not been carefully studied. It is probable that the compound obtained was identical with that described by Veley,<sup>1</sup> who prepared it by passing hydrogen bromide into glycerol. The boiling point recorded is 160° at 66 mm.

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## HALOGENATION. X. CHLORIC ACID AS A REAGENT IN ORGANIC CHEMISTRY.

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The preparation of organic chlorates has not been attempted with the exception of a few isolated instances. It was thought desirable to study the chlorates of organic bases systematically, as also the action of chloric acid on organic compounds in general.

Chlorates have been prepared either by the direct action of chloric acid on the organic base or by means of double decomposition between the hydrochloride of the base and silver chlorate. They form readily with the aliphatic bases according to either of the above methods, but in the case of aromatic bases the action is quite different. Sometimes the chlorate could not be formed at all since the base undergoes oxidation rapidly. With an excess of chloric acid, the decomposing bases form brown to yellow oily substances which consist, generally, of the lower chloroquinones. With regulated amount of chloric acid, the decomposing substances form dyes. It has also been found that iodo derivatives of

<sup>1</sup> *Jahresbericht d. Chemie*, 1883, 858.