

These observations are in accord with the idea that the effect of ethylene in the ripening of fruits and vegetables is primarily concerned with color change rather than a true ripening process.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 235]

A NEW TEST FOR DISTINGUISHING THE PRIMARY, SECONDARY AND TERTIARY SATURATED ALCOHOLS

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The most convenient method of distinguishing the three classes of alcohols is that given by Kamm,¹ who makes use of the difference in the rate with which the alcohols react with hydrobromic acid.

The readiness with which tertiary butyl alcohol reacts with cold concentrated hydrochloric acid² suggests this reaction as a means of distinguishing the tertiary alcohols.

Secondary but not primary alcohols react at room temperature with concentrated hydrochloric acid containing zinc chloride in the mole ratio of one to two. This reagent, which was first employed by Norris and Taylor³ at higher temperatures for the preparation of alkyl chlorides, has recently been used for preparing 2-chloro- and 3-chloro-3-ethylpentane from the corresponding alcohols at room temperature.⁴

Reagent.—The hydrochloric acid–zinc chloride reagent is made by dissolving 136 g. (1 mole) of anhydrous zinc chloride in 105 g. (1 mole) of concentrated hydrochloric acid with cooling. Either Baker's zinc chloride, fused sticks, or a technical powder may be used.

Procedure.—To 2 ml. of the alcohol in a vial or test-tube is quickly added 12 ml. of the hydrochloric acid–zinc chloride reagent at 26–27°. The mixture is shaken and the tube is closed with a cork. Alcohols lower than hexyl are soluble, but tertiary alcohols react so fast and the separation of the tertiary chloride proceeds so rapidly that two phases are observed from the time of mixing. On standing, within five minutes or less the clear solution becomes cloudy in the case of the secondary alcohols and undergoes no change other than darkening in the case of the primary. After one hour a distinct upper layer is visible in the case of all of the secondary alcohols except *isopropyl*. The results are shown in the table.

¹ Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, 1923; Kamm and Marvel, *THIS JOURNAL*, **42**, 299 (1920).

² Davis and Murray, *Ind. Eng. Chem.*, **18**, 844 (1926); "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 50.

³ Norris and Taylor, *THIS JOURNAL*, **46**, 753 (1924).

⁴ Lucas, *ibid.*, **51**, 248 (1929).

TABLE I

BEHAVIOR OF ALCOHOLS WITH HYDROCHLORIC ACID-ZINC CHLORIDE REAGENT AT 26°

Clear solutions		Clear solutions becoming cloudy within five minutes	
CH ₃ OH	C ₂ H ₅ OH	CH ₃ OHCH ₂ OH ^a	CH ₃ CHOHCH ₂ ^a
CH ₂ ClCH ₂ OH ^a	CH ₃ CH ₂ CH ₂ OH ^a	CH ₃ CHOHCH ₂ CH ₂ CH ₃ ^{a, c}	
CH ₃ (CH ₂) ₂ CH ₂ OH ^a	(CH ₃) ₂ CHCH ₂ OH ^a	CH ₃ CHOHCH(C ₂ H ₅) ₂ ^d	
(CH ₃) ₂ CHCH ₂ CH ₂ OH ^b		CH ₃ CH ₂ CHOHCH ₂ CH ₃ ^a	

^a Eastman's. ^b Merck's. ^c Stanco Distributors, New York, through the courtesy of Mr. C. L. Bowman. ^d Lucas, ref. 4.

To distinguish with certainty between tertiary and secondary alcohols, another sample of the alcohol is mixed with concd. hydrochloric acid alone. Tertiary butyl and amyl alcohols immediately react to form the insoluble chloride, which rises to the surface in a few minutes. The solutions obtained from the secondary alcohols should remain clear.

Discussion.—With the exception of the unsaturated primary alcohol, allyl, which reacted within seven minutes, none of the primary alcohols tried gave the test with the zinc chloride-acid mixture, while all of the secondary did. Even though the alcohol does not mix with the reagent, it is still possible to distinguish between those which react and those which do not, since in the former case the aqueous phase takes on a milky appearance due to the separation of the finely divided chloride. Thus both 1-hexanol and 2-hexanol gave two phases, but only in the case of the latter did the lower phase take on the cloudy appearance characteristic of the reaction. The secondary alcohol, 3-ethyl-2-pentanol, behaved like the tertiary alcohols in that the chloride separated within one or two seconds after mixing.

In carrying out these tests with the alcohols the production of the second phase cannot be taken as the sole criterion of the reaction; the formation on standing of a distinct upper layer must be an accompanying phenomenon.⁵ For example, a 20% solution of 2-butanol in 1-butanol gave a slight cloudiness within six minutes at 26°; this increased somewhat on standing. However, even after ten hours there was no distinct upper layer but only a few small drops of a second phase made visible by gentle agitation. A 10% solution of 2-butanol in 1-butanol gave a slight cloudiness in thirty minutes, increasing on standing. With concentrated hydrochloric acid alone a 10% solution of tertiary butanol in 2-butanol give an immediate cloudiness, one of 5% reacted in thirty seconds, while one of 4% failed to give the test. In none of these cases was an upper layer apparent. It is thus evident that when the reaction proceeds so as to produce a cloudiness without the upper layer developing, an alcohol is present as an impurity.

⁵ The upper layer did not form with *isopropyl* alcohol, presumably because of the volatility of the chloride.

Apparently, some of the alcohols used in this work were not of the highest purity, since the 2-propanol, 2-pentanol and 3-pentanol gave weakly cloudy solutions with concd. hydrochloric acid alone. However, the tests for distinguishing the alcohols as developed herein are believed to be reliable, since the amounts of these impurities were small.

The reaction time is lower if the proportion of reagent to alcohol is smaller, or if the temperature is lower. At a six to one ratio 2-butanol gave the test in two minutes at 26° and in seven minutes at 20°; at a four to one ratio, in five and nine minutes, respectively; while at a two to one ratio (approximately mole per mole) the test was given in two and one-half to three hours.

Summary

The lower saturated alcohols may be readily differentiated by the fact that the tertiary alcohols react rapidly with concentrated hydrochloric acid alone to form insoluble liquid chlorides, the secondary react with hydrochloric acid-zinc chloride mixture within five minutes at 26°, while the primary alcohols react with neither. Allyl alcohol resembles a secondary alcohol.

The presence of a secondary or a tertiary alcohol in another compound may be demonstrated by these reagents, provided the concentration of the alcohol is not too low.

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SYNTHESIS OF N-PHENYLPYRROLIDINE AND N-HEXAHYDROPHENYLPYRROLIDINE

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In a study of the insecticidal action of nicotine and related compounds, pyrrolidine and a series of its derivatives were desired. The methods reported in the literature¹ for the preparation of pyrrolidine are all difficult and tedious. During the progress of the studies reported below, Anderson and McElvain² published their work on the catalytic reduction of pyrrole using specially purified pyrrole, glacial acetic acid, a large quantity of platinum-oxide platinum black catalyst and shaking for four to five days.

The catalytic reduction is much more convenient with the platinum-oxide platinum black catalyst using as a solvent absolute alcohol contain-

¹ Ciamician and Magnaghi, *Ber.*, **18**, 2079 (1885); Ladenburg, *ibid.*, **19**, 780 (1886); **20**, 2215 (1887); Wohl, Schafer and Theile, *ibid.*, **38**, 4157 (1906); Gabriel, *ibid.*, **42**, 1254 (1912); Keil, *ibid.*, **59**, 2816 (1926); Putochin, *ibid.*, **55**, 2742 (1922); Willstätter and Hatt, *ibid.*, **45**, 1477 (1912); Willstätter and Waldschmidt, *ibid.*, **54**, 125 (1921); Hess, *ibid.*, **46**, 3113 (1913).

² Anderson and McElvain, *THIS JOURNAL*, **51**, 887 (1929).