

culatation was undertaken. From the numerous examples in Table I, it is possible to calculate approximate contributions of acetylenic carbon (C^\equiv) and of the α , β , γ , . . . , ω carbon atoms combined thereto, assuming only that hydrogen is normal, *i. e.*, contributes 1.100 per atom. On this basis there is obviously no correction for the triple bond. The various calculations are best explained by the following examples. The observed refraction for 1-pentyne less 1.100 gives 22.018 as the value for the group $CH_3-CH_2-CH_2-C\equiv C-$; one-half the observed value for 4-octyne, 18.754, is the contribution of $CH_3-CH_2-CH_2-C\equiv C-$. Thus one C^\equiv contributes 3.264, the difference between 22.018 and 18.754. Similar calculations made by comparison of 1-hexyne with 5-decyne and of 3,3-dimethyl-1-butyne with 2,2,5,5-tetramethyl-3-hexyne give C^\equiv values of 3.293 and 3.163, respectively. The maximum deviation is only 0.130 and the average of the three values, 3.240, is now taken as the mean contribution of one acetylenic carbon atom, C^\equiv .

The value for *alpha* carbon atoms, C^α , was calculated from the data for 2-butyne: MR (obsd.), 18.637; C^\equiv , 3.240; H, 1.100; C^α (calcd.), 2.779.

In a similar way the average contribution of *beta* carbon atoms was obtained from the data for 2-pentyne, 3-hexyne, 3,3-dimethyl-1-butyne, and 2,2,5,5-tetramethyl-3-hexyne. The values so found are 2.606, 2.583, 2.608, and 2.624, respectively; average 2.605.

Using these average values, the increment for each C^γ was estimated from the observed refractions of 1-pentyne, 4-octyne, and 3-methyl-3-ethyl-4-heptyne. The agreement is again surprisingly good, the values being 2.454, 2.430, and 2.423, respectively; average, 2.436.

It is seen immediately that the succeeding carbon atoms rapidly approach the normal mean value, 2.418, and it may be assumed that the C^δ ... ω increments are, indeed, 2.418 units each. Not only is it likely that the atomic exaltations induced by the triple bond should be largely dissipated at the *delta* carbon atoms, it is possible to justify this assumption by noting the increments for succeeding methylene units in the symmetrical dialkylacetylenes: $C_2H_5-C\equiv > CH_3-C\equiv$, 4.783; $n-C_3H_7-C\equiv > C_2H_5-C\equiv$, 4.652; $n-C_4H_9-C\equiv > n-C_3H_7-C\equiv$, 4.619; $n-C_5H_{11}-C\equiv > n-C_4H_9-C\equiv$, 4.616; accepted, $-CH_2-$, 4.618.

The final atomic refractions recommended for alkyl and dialkylacetylenes are, therefore, C^\equiv 3.240; C^α , 2.779; C^β , 2.605; C^γ , 2.436; C^δ ... ω , 2.418; H, 1.100.

The comparison of molecular refractions, observed and calculated on the old and present basis, is made in Table I. The agreements for the present method are uniformly quite good, the maximum deviation being about 0.5%. The normal acetylenes check particularly well; the

highly branched isomers deviate slightly in proportion to the extent of branching.

An alternative method of calculation which has been employed commonly with other types of compounds is the use of alkyl group values determined from known compounds. The examples in Table I make possible the assignment of group values for methyl, ethyl, *n*-propyl, *n*-butyl, *t*-butyl, and a few others in the usual manner. Unfortunately, however, such group values taken from several examples frequently disagree. Thus the contribution for *t*-butyl calculated from *t*-butylacetylene is 19.749; taken from di-*t*-butylacetylene it is 20.204, both values based on 2.398 for the triple bond correction. It seems better, therefore, to calculate the expected molecular refraction by summation of the average contributions of the various types of atoms in the molecule.

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The Preparation of Some Tertiary Alcohols by the Addition of Organic Acids to Grignard Reagents

BY RALPH C. HUSTON AND DONALD L. BAILEY

In 1904, Grignard¹ prepared 2-methyl-5-ethyl-5-heptanol by passing carbon dioxide into isoamylmagnesium bromide and adding ethylmagnesium bromide to the reaction mixture. He also prepared 2,7-dimethyl-5-isobutyl-5-nonanol from isobutylmagnesium bromide and isoamylmagnesium bromide. Later Iwano² used the method to prepare 5-butyl-5-nonanol.

A patent³ issued to Bayer and Company in 1906 covered the preparation of tertiary alcohols from organic acids (or their potassium salts) but gave little detail as to procedure or yield.

We have prepared the following sixteen tertiary alcohols in 40-60% yield by slowly adding one mole of organic acid in ether to 3,3 moles of primary Grignard reagent⁴ and refluxing on a water-bath for two hours: 2-methyl-2-pentanol, 2-methyl-2-hexanol, 3-ethyl-3-hexanol, 2-methyl-3-ethyl-3-pentanol, 3-ethyl-3-heptanol, 3-ethyl-5-methyl-3-hexanol, 3-ethyl-3-octanol, 6-methyl-6-undecanol, 6-ethyl-6-undecanol, 6-propyl-6-undecanol, 6-isopropyl-6-undecanol,⁵ 6-butyl-6-undecanol, 6-isobutyl-6-undecanol,⁶ 6-amyl-6-undecanol and 5-butyl-5-nonanol. (The yield of 2-methyl-2-propanol was 4% and that of 3-methyl-3-pentanol was 32%.)

It was found that yields of the alcohols could be increased by adding the acid in benzene solution

(1) Grignard, *Compt. rend.*, **138**, 154 (1904).

(2) Iwano, *Bull. soc. chim.*, **82**, 244 (1925).

(3) German Patent 166,898-99 (1906).

(4) Whitmore and Badertscher, *THIS JOURNAL*, **55**, 1561 (1933).

(5) B. p. 104-106° (2 mm.); d_4^{20} 0.8425; n_D^{20} 1.4477. Calcd. for $C_{14}O_{10}$: C, 78.5; H, 14.02. Found: C, 78.41; H, 14.17.

(6) B. p. 116-118° (3 mm.); d_4^{20} 0.8367; n_D^{20} 1.4464. Calcd. for $C_{14}H_{26}O$: C, 78.95; H, 14.04. Found: C, 78.63; H, 14.14.

(200 ml. per mole of acid), distilling off the ether until the temperature reached 83° and then refluxing for two hours. For example, when this method was used, the yield of 2-methyl-3-ethyl-3-pentanol was 70% instead of 53%.

The addition of the second molecule of alkylmagnesium halide to the salt and subsequent elimination of oxymagnesium halide was relatively slow. Less than fifteen per cent. of ketone was formed from butyric acid and *s*-butylmagnesium bromide, and less than two per cent. from the same acid and *t*-butylmagnesium bromide.

The addition of the final molecule of primary Grignard is more rapid but there was always a considerable amount (10–20%) of ketone in the reaction product. Attempts to prepare ketones by adding two moles of primary Grignard reagent to one of the acid gave, as the main product, the tertiary alcohol. This final step gave less than one per cent. of tertiary alcohol in the cases of secondary butyl and tertiary butyl Grignard reagents.

In all cases where primary Grignard reagents were used, the same colorless crystalline salt separated from the reaction mixture after most of the acid had been added. (It did not separate when acids were added to secondary or tertiary butylmagnesium bromide.) The ether was decanted off. The crystals were washed with anhydrous ether and dried in a vacuum desiccator over sulfuric acid. Analysis and reactivity shows a complex made up of one molecule and $\text{BrMg}\cdot\text{OMgBr}$, two molecules of MgBr_2 and four molecules of ether.

Anal. Calcd. for $\text{C}_{16}\text{H}_{40}\text{O}_5\text{Mg}_4\text{Br}_6$: Mg, 10.93; Br, 54.0; equiv. wt., 444.5. Found: Mg, 10.90; Br, 53.93; equiv. wt., 447.

When treated with water, the double salt decomposed rapidly and gave off ether. A sample was hydrolyzed. Concentration of the filtered solution gave $\text{MgBr}_2\cdot 6\text{H}_2\text{O}$.

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The Alcoholysis of Cellulose¹

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AND JOEL E. GIDDENS²

Although acid-catalyzed hydrolysis of cellulose has been the subject of numerous investigations, the alcoholysis of cellulose seems to have received less attention. Hibbert and co-workers,³ Brown,

(1) From Southern Regional Research Laboratory, New Orleans, Louisiana. One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

(2) Resigned January 3, 1945.

(3) L. Brickman, W. L. Hawkins and H. Hibbert, *THIS JOURNAL*, **62**, 2149–2154 (1940); W. B. Hewson, J. L. McCarthy and H. Hibbert, *ibid.*, **63**, 3041–3045 (1941); **63**, 3045–3048 (1941); E. West, W. S. MacGregor, T. H. Evans, I. Levi and H. Hibbert, *ibid.*, **65**, 1176–1180 (1943); K. A. West, W. L. Hawkins and H. Hibbert, *ibid.*, **63**, 3038–3041 (1941).

Heddle and Gardner,⁴ and unpublished investigations by Ambler⁵ have been concerned chiefly with the non-cellulosic substances which pass into solution upon alcoholysis of wood or other cellulosic materials. Pulping with alcohols has been studied,⁶ but the conditions were unfavorable for acid-catalyzed alcoholysis and the products did not resemble those described below. Mark and Siggia⁷ encountered the alcoholysis of modified "carboxy cellulose," but their interest was principally concerned with the esterification of carboxyl groups, not in the cleavage of the glucosidic linkages.

In hydrolysis of cellulose certain glucose-glucose linkages are ruptured with addition of a molecule of water. It was anticipated that alcoholysis would result in rupture of glucose-glucose bonds with the addition of a molecule of alcohol. This conception of the reaction seems to receive confirmation in the experiments described below.

Alcoholized cellulose differs from hydrocellulose in a number of ways: It is stable toward hot aqueous alkali, is non-reducing by the copper number determination, and it contains measurable amounts of alkoxyl groups attached by glycosidic (acid labile) linkages. Although degradation of cellulose appears to be more rapid by alcoholysis than by hydrolysis, it is found that approximately the same upper limit of fluidity is reached in each instance.

Experimental

Rate of Alcoholysis.—Parallel experiments were set up employing 0.5 *N* hydrochloric acid in methanol, ethanol, methanol-water (9:1 by volume), and water. Commercial grades of absolute methanol and ethanol were used without further purification. Samples of cotton fiber⁸ were placed in glass-stoppered flasks containing 30 volumes of one of the acid solutions. After having been allowed to stand various lengths of time in a thermostat at 20°, the samples were removed, filtered on sintered glass filters, rinsed with water until free from acid, and allowed to dry in air. The recovery of fiber was greater than 95% in all instances. The results of fluidity measurements⁹ on the products from the experiments with absolute methanol, 90% methanol, and water are shown in Fig. 1. Inspection of this figure shows that the rate of degradation is greatest for absolute methanol, intermediate for the

(4) J. S. Brown, R. D. Heddle and J. A. F. Gardner, *ibid.*, **62**, 3251–3252 (1940).

(5) J. A. Ambler, private communication.

(6) S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.*, **28**, 1270–1276 (1936); **29**, 1431–1434 (1937); H. Y. Charbonnier, *Paper Trade J.*, **114**, No. 11, 31–36 (1942).

(7) H. F. Mark and S. Siggia, U. S. Patent 2,379,917, July 10, 1945.

(8) The cotton fiber used in this work had been mechanically cleaned in a Shirley Analyzer. It was extracted in a Soxhlet extractor for four hours with alcohol and boiled for eight hours with water. The cotton linters used in some experiments had been purified by a commercial firm. The fibers and linters were used in the air-dried condition, it having been found in separate experiments that the small amount of moisture introduced with the sample did not cause a detectable change in the course of the reaction.

(9) Fluidity measurements were made at 25° in British Fabrics Research Committee type viscometers (see "The viscosity of cellulose solutions," H. M. Stationery Office, London, 1932). The cuprammonium solvent contained 15 ± 0.1 g. of copper and 240 ± 5 g. of NH_3 per liter. The dispersions contained 0.5 g. anhyd. fiber per 100 ml. and the results are expressed in rhes.