

## A REVISION OF THE PENTANOLS.

BY S. M. GORDON.

*(Continued from p. 224.)*

## THE INDIVIDUAL ALCOHOLS.

1. Pentanol-1.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ .*Synonyms.*— $\alpha$ -oxy-pentane

Butyl carbinol

Primary normal amyl alcohol

Normal amyl alcohol

*History.*—In 1871, Lieben and Rossi (*Ann.*, 159, 70 (1871)) prepared normal valerianic acid for the first time, by the hydrolysis of *n*-butyl cyanide. The acid was converted to the aldehyde by dry distillation with calcium formate. The aldehyde was then reduced by sodium amalgam and  $\text{H}_2\text{SO}_4$  (cp. Lieben and Rossi, *Ann.*, 158, 150 (1871)) to the corresponding alcohol, pentanol-1. The constitution of the body follows from the method of preparation.

*Methods of Formation.*—*a.* By reduction of *n*-valeric aldehyde with sodium amalgam (Lieben and Rossi, *Ann.*, 159, 70 (1871)).

*b.* By reduction of ethyl valerate with sodium ethylate (Bouevault and Blanc, French Pat. through *Central*, 76, 2, 1700 (1905)).

*c.* By treating *n-p*-amyl amine with nitrous acid (Gartenmeister, *Ann.*, 233, 253 (1886)).

*Preparation.*—Reduction of ethyl *n*-valerate with sodium gives 56–61% of the alcohol (Adams, Kamm and Marvel, *Univ. of Illinois Bull.*, Vol. 18, No. 6, p. 54 (Oct. 11, 1920)).

*Occurrence.*—Small amounts result from the action of bacillus butylicus on glycerol (Morin, *Bull. de Soc. Chem.* (2), 48, 803 (1887)).

In the "yellow oil" from butyl alcohol fermentation of starch (Marvel and Broderick, *J. A. C. S.*, 47, 3045 (1925)).

*Identification.*—Being a primary alcohol it would be expected that the compound might be identified by oxidation to the corresponding aldehyde and hence preparation of an oxime or semicarbazone. A survey of the literature, however, shows that no report has been made on the preparation of an aldehyde by oxidation from this alcohol. However, the aldehyde prepared in a different manner yields an oxime of m. p.  $52^\circ$  (Blaise, *Compt. rend.*, 138, 698 (1904)). No record of the semicarbazone has been found. Complete oxidation would lead to the acid, which could be converted into a silver salt and thus identified. This has been done by Fournier (*Bull. de Soc. Chem.* (4), 5, 923 (1909)), but the inherent difficulty of this method is that it does not distinguish between the four isomeric primary pentanols, as each would be oxidized to an acid and all having the same molecular weight. Hence other methods were adopted.

The earliest method thus used was interaction with phenyl isocyanate to yield the corresponding phenyl urethane. The melting point of the phenyl urethane is given as  $46^\circ\text{C}$ . by Blaise and Picard (*Ann. Chem. et Phys.* (8), 25, 261 (1912)).

Analogous to phenyl isocyanate is  $\alpha$ -naphthyl isocyanate. This reacts more readily than the phenyl compound, hence has come in great favor for identification

of the alcohols. The  $\alpha$ -naphthyl urethane of normal amyl alcohol melts at 66–67° (see chapter on  $\alpha$ -naphthyl urethanes).

The 3,5-dinitro-benzoate of normal primary amyl alcohol melts at 45° C. (see chapter on 3,5-dinitro-benzoates).

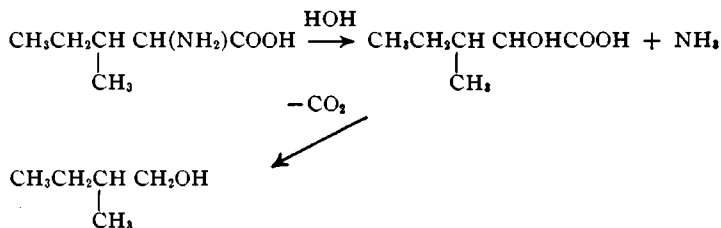
The 3-nitro-phthalic acid ester melts at 133° (Marvel and Broderick, *J. A. C. S.*, 47, 3045 (1925); cp. chapter on 3-nitro-phthalates).

2. Methyl-2-butanol-1.  $\text{CH}_3\text{CH}_2\overset{*}{\text{C}}\text{HCH}_2\text{OH}$ .



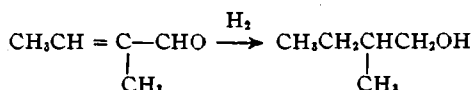
*Synonyms.*—Secondary butyl carbinol  
Methyl ethyl carbin carbinol  
Active amyl alcohol  
Dextrogyrate amyl alcohol

*History.*—Secondary butyl carbinol is an essential constituent of fusel oil, which was recognized by Scheele in 1785. That a body having the power of rotating the plane of polarized light was present in fusel oil was early recognized by Biot (*Compt. rend.*, 41, 296 (1855)). Pasteur (*Compt. rend.* 41, 296 (1855)), found that the degree of rotation of the fusel oils depended on the source. This led him to believe that the amount of the active constituent depended on the conditions of formation. He further showed that the optically active body could be separated from the inactive body accompanying it in fusel oils by the formation of the amyl sulphuric esters, which could then be separated by repeated fractional crystallization of the barium salts, subsequently formed. In a critical study of the separation of the constituents of fusel oil Marckwald (*Ber.*, 34, 479 (1901); 35, 1598 (1902); 37, 1039 (1904)), confirmed the results of Pasteur and placed the chemical separation of the 2-methyl-butanol-1 and 2-methyl-butanol-4 on a satisfactory basis. Marckwald used the method devised by Le Bel (*Compt. rend.*, 77, 104 (1873)), and the formation of the 3-nitro-acid phthalates to separate these isomers. Later, F. Ehrlich (*Ber.*, 40, 1035 and 2251 (1907)) showed that isoleucine, when acted on by yeast in the presence of cane sugar yielded the alcohol in question—in quantitative yields. Further investigations showed that the amount of methyl-2-butanol-1 and methyl-3-butanol-1 in fusel oil from molasses spirit depended on the amount of isoleucine (3-methyl-2-amino pentane acid 1) and leucine originally present. This led to the amino-acid theory for the formation of the amyl alcohols. That is the alcohols are presumed to form according to the following scheme:



*Methods of Formation.*—a. From isoleucine by yeast in the presence of cane sugar (Ehrlich, *Ber.* 40, 2251 (1907)).

b. By reduction of tiglic aldehyde by iron and acetic acid. (Lieben and Zeissel, *Monats.*, 7, 60 (1886).)



*c.* By treating 2-bromo-butane with magnesium and formaldehyde (Freundler, *Bull. de Soc. Chim.* (3) 35, 110 (1906)). Methods *b* and *c* yield inactive mixtures.

*Preparation.*—*A.* By separation from fusel oil.

1. The barium salts of the acid sulphuric esters are prepared and separated by fractional crystallization. The alcohol is regenerated from the barium salt by dilute sulphuric acid (Pasteur, *loc. cit.*; Marckwald, *loc. cit.*).

2. The mixture of alcohols is esterified with dry HCl gas. The inactive form (2-methyl-butanol-4) is more readily attacked. The chloride of the active form is separated by distillation. Repetition of the process gives an alcohol of high rotation, but not an absolutely pure product (Le Bel, *loc. cit.*; also Plimpton, *J. A. C. S.*, 39, 332 (1881); Guye, *Ann. chim. phys.* (6) 25, 174 (1892)).

3. The mixture of alcohols is esterified with 3-nitro-phthalic acid and the resultant acid phthalates separated by fractional crystallization. The esters are then saponified with dilute alkali. This method gives a very pure product (Marckwald and McKenzie, *Ber.*, 34, 485 (1901), and 37, 1039 (1904)).

*B.* By synthesis.

2-Bromo-butane with formaldehyde by Grignard's reaction gives 73% of the inactive form (Freundler, *loc. cit.*).

*Occurrence.*—Methyl-2-butanol-1 is found in:

- Potato and grain fusel oil (Marckwald, *Ber.*, 34, 479 (1901)).
- In corn fusel oil (Rudakow, *Central*, 1, 1481 (1904)).
- In molasses spirit (Ehrlich, *loc. cit.*, and Kaillan, *Monats.*, 24, 533 (1903)).
- In "yellow oil" from butyl alcohol fermentation (Marvel and Broderick, *J. A. C. S.*, 47, 1034 (1925)).

*Identification.*—Secondary butyl carbinol being a primary alcohol, hence on oxidation it would be expected to yield the corresponding aldehyde and acid, which could then be identified either by the usual methods for aldehydes and acids, respectively. But F. Ehrlich (*Ber.*, 40, 2556 (1907)), has shown that careful oxidation leads to a very low yield of the corresponding aldehyde. The optically active aldehyde does not form an oxime, but the inactive form yields a liquid oxime of b. p. 149–151° (Neustadter, *Monats.*, 27, 1884 (1906)). The semicarbazone prepared from the aldehyde melts at 103° C. (Sommelet, *Bull. de Soc. Chem.* (4), 1, 406 (1907)).

Complete oxidation to the acid must be carried out with great care. Marckwald (*Ber.*, 37, 1045 (1904)) and Lieben and Zeissel (*Monats.*, 7, 60 (1886)), obtained different results, both using  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$ . Marckwald was able to identify only the corresponding acid, while the latter workers obtained not only the acid corresponding to that alcohol but also  $\text{HCOOH}$  and  $\text{CH}_3\text{COCH}_2\text{CH}_3$ . Hence more satisfactory methods than the older ones are advisable.

These were found in such crystalline derivatives as the phenyl urethanes,  $\alpha$ -naphthyl urethanes, 3,5-dinitro-benzoic acid esters and the 3-nitro-phthalic acid esters. The properties of the compounds were redetermined as part of this investigation.

Phenyl urethane of the active form m. p. 30°, of the inactive form m. p. 31° (Marckwald, *Ber.*, 37, 1049 (1904).

$\alpha$ -Naphthyl urethane, m. p. 82° (Neuberg and Kansky, *Biochem. Z.*, 20, 445 (1909)).

3.5-Dinitro-benzoate, m. p. 83–84° (see chapter on 3.5-dinitrobenzoates).

3-Nitro-phthalic-acid ester, m. p. 159° (Nicollet and Sacks, *J. A. C. S.*, 47, 2384 (1925); also see chapter on 3-nitro-acid-phthalates of this report).

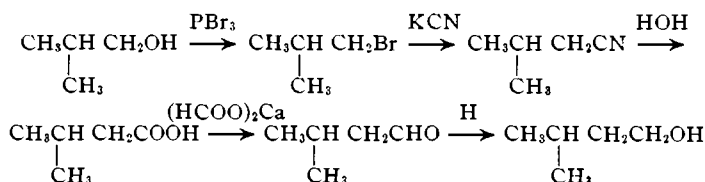
### 3. Methyl-3-butanol-1 $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$



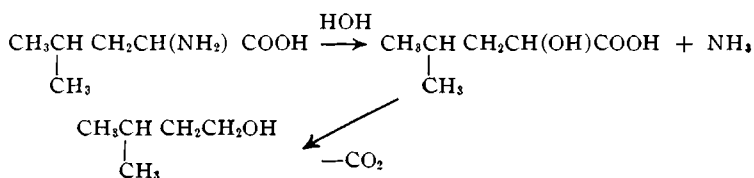
*Synonyms.*—Isobutyl carbinol  
Primary isoamyl alcohol  
Isoamyl alcohol  
Fermentation amyl alcohol

*History.*—Methyl-3-butanol-1 is closely connected with methyl-2-butanol-1. It is the chief constituent of the fusel oils. It occurs with its isomer, optically active amyl alcohol in all the fusel oils thus far investigated. The fusel oil of which this is the chief constituent was recognized as early as 1775 by Scheele in the "Nachlauf" of spirit distillation. The properties of a constant boiling fraction of fusel oil of boiling point 130–132° was investigated by Dumas, Cohours and others (see introduction). As a result of these investigations, it was found that the constant boiling portion had the formula  $\text{C}_5\text{H}_{12}\text{O}$  and belonged to the series of alcohols of which ethyl alcohol was the chief member. Biot (*Compt. rend.*, 41, 295 (1855)), later showed that the "alcohol" thus isolated rotated the plane of polarized light. With the advent of the asymmetric carbon theory of Van't Hoff and Le Bel (1874), it was assumed that the mixture of alcohols must contain one with an asymmetric carbon atom. Pasteur, earlier (*Compt. rend.*, 41, 296 (1855)), found that the degree of rotation of the "alcohol" depended on the source of the fusel oil. From now on the question of the existence of this alcohol is closely linked with that of its isomer. Studies by Pasteur, Le Bel and critical studies of Marckwald showed methods for the separation of this alcohol from its accompanying isomer by fractional crystallization of the barium salts of ethyl sulphuric acid, of the 3-nitro-acid phthalates and by rate of esterification with hydrochloric acid gas.

The formula assigned to the alcohol was confirmed by synthesis of the alcohol from isopropyl carbinol by the following reactions (Erlenmeyer, *Ann. sup.*, 5, 337 (1867)).



F. Ehrlich (*Ber.*, 40, 1035 and 2251 (1907)) showed that this alcohol could be derived from leucine; methyl-4-amino-2-pentane acid (5), by the action of yeast in a sugar medium. This led to the amino-acid theory of amyl alcohol formation. This would be expressed as follows:



Derivatives prepared from "amyl alcohol," that is a mixture of the two isomers have unfortunately been designated as amyl alcohol derivatives. Hence there appears to be a vital need to revise the constants in this regard. Many of the physical properties thus listed in the literature are not trustworthy.

*Formation.*—*a.* See under history.

*b.* From leucine (Ehrlich, *loc. cit.*; and Pringsheim, *Biochem. Z.*, 8, 128 (1908)).

*c.* Reduction of the aldehyde:

1. By sodium amalgam (Friedel, *Ann.*, 124, 326 (1862)).

2. By calcium hydroxide (Fittig, *Ann.*, 114, 66 (1860)).

*Preparation.*—I. *From fusel oils:*

*a.* By fractional crystallization of the barium salts of amyl sulphuric acids (Marckwald, *Ber.*, 34, 479 (1901); 35, 1598 (1902) and 37, 1039 (1904)).

*b.* By esterification with HCl (see under preparation of 2-methyl butanol-1).

*c.* By esterification with 3-nitro-phthalic acid (see under preparation of 2-methyl-butanol-1).

II. From leucine (Ehrlich, *loc. cit.*).

III. By synthesis.

From methyl-2-chloro-3-pentane with Grignard's reagent and polymethylene in 50% yields (Locquin, *Bull. de Soc. Chim.* (3), 31, 599 (1904)).

*Occurrence.*—In fusel oils of different origins (Marckwald, *Ber.*, 34, 479 (1901)).

In acorn (Rudikow and Alexandrow, *J. Russ. Phys.-Chem. Ges.*, 36, 207 (1904); through *Central*, 75, 1481 (1904)).

In molasses spirit (Ehrlich, *Ber.*, 40, 1044 (1907)).

In wood-tar oil (formation and analysis of acetyl and benzoyl esters) (Looft, *Ann.*, 275, 369 (1893)).

As an ester in Roman chamomile oil (*Anthemis nobilis*) saponification and preparation of the phenyl urethane (Blaise, *Bull. soc. chim.* (3), 29, 329 (1903)).

In *Eucalyptus globulus* and *Eucalyptus amydalina* oils (Bouchardat, *Bull. soc. chim.* (3), 9, 429 (1893)).

In Grasse peppermint oils, oxidation to the acid (Roure Bertand, *Fils. Reports*, (2), 9, 29 (1909)).

In American peppermint oil (Power and Kleber, *Pharm. Rund.*, 12, 157 (1894)).

In Valencia orange oil, oxidation and analysis of the silver salt (Hall and Wilson, *J. A. C. S.*, 47, 2575 (1925)).

In Lavender oils, b. p. 129–133° and phenylurethane, m. p. 39–41°, "Gildermeister-Hoffmann, *Die Aetherische Oele*," Vol. 3, 439.

In the "yellow oil" from butyl alcohol fermentation (Marvel and Broderick, *J. A. C. S.*, 47, 3045 (1925)).

In the essential oil of the cotton plant (Power and Chestnut, *J. A. C. S.*, 47, 1751 (1925)).

The amount of the isomeric pentanols in fusel oils has been studied in more recent times by Windisch (*Arbeit. aus der Kais. Gesundheitsam.*, Berlin, 8, 214 (1894)).

*Identification.*—Being a primary alcohol it is expected to be oxidized either to the corresponding aldehyde or acid. Oxidation with chromic acid mixture leads to the formation of both the acid and the aldehyde. The aldehyde has been prepared by Tollens (*Ber.*, 36, 1342 (1903)) and by Kohn (*Monatsh.*, 17, 127 (1896)). It gives a liquid oxime of boiling point 161° C. (Cihlor, *Monatsh.*, 25, 158 (1904)).

Oxidation with  $\text{KMnO}_4$  in alkaline solution leads to the acid (Fournier, *Compt. rend.* 144, 333 (1907)). This can then be converted into the corresponding silver salt and analyzed.

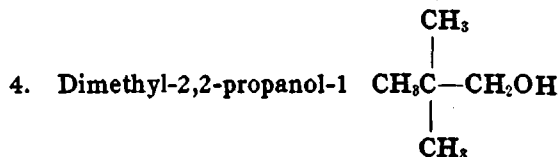
The crystalline derivatives which have been prepared and may be used for identification are herewith reported.

Phenyl-urethane, m. p. 55° (Marckwald, *Ber.*, 37, 1049 (1904)).

$\alpha$ -Naphthyl urethane, m. p. 67–68° (Neuberg and Kansky, *Biochem. Z.*, 20, 445 (1909)), m. p. 61° (see chapter on  $\alpha$ -naphthyl-urethanes).

3,5-Dinitro-benzoate, m. p. 61° (see chapter on 3,5-dinitro-benzoate).

3-Nitro phthalic acid ester, m. p. 164° (Nicollet and Sacks, *J. A. C. S.*, 47, 2348 (1925); also see chapter on 3-nitro-phthalic acid esters).



*Synonyms.*—2,2-Dimethyl-propanol-1  
Tertiary-butyl-carbinol  
Tertiary-primary-amyl-alcohol

*History.*—Relatively little is known of the properties of this alcohol. It was first prepared by Tissier (*A. Ch.* (6), 29, 340 (1893)), and its oxidation products studied. The best yield obtainable has been 4% (Samec, *Ann.*, 351, 256 (1907)). It is the only solid pentanol known (m. p. 48° C.).

*Formation and Preparation.*—*a.* Reduction of a mixture of trimethyl acetic acid chloride and trimethyl acetic acid with sodium amalgam (Tissier, *loc. cit.*).

*b.* Reduction of trimethyl acetaldehyde with sodium (Tissier, *loc. cit.*).

*c.* The action of sodium ethylate on trimethyl acetamide (Scheuble, *Monatsh.*, 25, 1099 (1904)).

*d.* By Grignard's reaction, magnesium and paraformaldehyde on tertiary butyl bromide (yields, 4%) (Samec, *Ann.*, 351, 256 (1907)).

*Oxidation.*—Oxidation of the alcohol with dichromate mixture gives a mixture of trimethylacetaldehyde, methyl-isopropyl-carbinol, and trimethyl-acetic-acid (Tissier, *loc. cit.*; cp. Samec, *loc. cit.*).

*Occurrence.*—This alcohol has not been reported in either the animal or vegetable kingdom.

*Identification.*—No solid derivatives of this alcohol are described in the literature.

The aldehyde formed by oxidation of the alcohol may be identified as the semi-carbazone; which melts at 192° C. (Bouevault, *Bull. de Soc. Chem.* (3), 31, 1326 (1904)).

5. **Pentan-ol-2**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ .

*Synonyms.*— $\beta$ -Oxy-pentane  
Methyl-propyl-carbinol  
Secondary normal amyl alcohol

*History.*—This alcohol was first prepared by Wurtz (*Ann.*, 148, 132 (1868)), by acting upon iodo-2-pentane with silver acetate and hydrolyzing the resultant ester with caustic potash. The constitution of the alcohol follows from the method of formation.

The alcohol contains an asymmetric carbon atom hence is expected to exist in two forms. Very little is known of the optically active isomers. Only one attempt at resolution appears in the literature. Le Bel (*Jahrs. ueber Fort. der Chem.*, 492 (1879)), found that *Pencilium glaucum*, developed in the racemic mixture attacked only the dextrogyrate form. The resultant alcohol showed a rotation of  $-12^\circ 33'$  in a 22-cm. tube.

The speed of esterification of this alcohol with trichloroacetic acid was studied by Michael and Wolgast (*Ber.*, 42, 3166 (1909)), who found its rate of esterification was in agreement with the secondary alcohol nature of the compound.

*Methods of Formation.*—*a.*  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHICH}_3 + \text{AgOCOCH}_3 \xrightarrow{\text{KOH}}$   
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHOCOCH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHOHCH}_3$  (Wurtz, *Ann.*, 148, 132 (1868)), and Bulohoubek (*Ber.*, 9, 925 (1876)).

*b.*  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHICH}_3 + \text{Pb}(\text{OH})_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHOHCH}_3$  (Wagner, *Ann.*, 179, 319 (1875)).

*c.* 1.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3 + (\text{NaHg})x \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHOHCH}_3$  (Friedel, *Jahrs. ueber Fort. der Chem.*, p. 513 (1869); Clarke, *Am. Chem. J.*, 39, 90 (1908)).

2.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3 + \text{H}_2(\text{Ni}) \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHOHCH}_3$  (Sabatier and Senderens, *Compt. rend.*, 137, 302 (1903)).

From  $\text{CH}_3\text{MgI}$  and normal butyric aldehyde. (Unpublished notes, Research Laboratory, Eastman Kodak Co.)

*Identification.*—As is well known secondary alcohols on oxidation yield the corresponding ketones, which could be isolated and identified as oximes, hydrazones or semi-carbazones, etc. .

Oxidation of the alcohol with alkaline  $\text{KMnO}_4$  yields not only the corresponding ketones, but also acetic and propionic acids (Wurtz, *Ann.*, 148, 133 (1868)). The ketone forms a liquid oxime (Trapesonzjanz, *Ber.*, 26, 1433 (1893)), which boils at 167° C.; and a semicarbazone melting at 100° (Scholtz, *Ber.*, 29, 611 (1896)).

However when diethyl carbinol is oxidized with  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$  not only does diethyl ketone form, but the ketone corresponding to the alcohol under discussion is also formed. The authors, however, do not state the yield obtained (Wagner and Saizew, *Ann.*, 179, 332 (1875)).

No record of any solid derivatives of this alcohol appears in the literature. The following solid derivatives have been prepared and characterized.

The phenyl-urethane melts at 34°.

The  $\alpha$ -naphthyl-urethane melts at 76°.

The 3,5-dinitro-benzoate melts at 60°.

The 3-nitro-acid-phthalate melts at 102–103°.

6. Pentanol-3  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ .

*Synonyms.*— $\gamma$ -Oxy-pentane

Diethyl carbinol

*History.*—The preparation of this compound was undertaken by Wagner and Saizew in 1875 (*Ann.*, 175, 351) to complete the series of alcohols of the formula  $\text{C}_5\text{H}_{12}\text{O}$  as required by Kolbe's theory (see general part). Then, only five of the eight required alcohols were known. The history of the isomeric pentanols up to this time is well reviewed by Wagner and Saizew (*Ann.*, 175, 351 (1875)).

*Methods of Formation.*—*a.* Ethyl formate is acted upon by zinc and ethyl iodide and the resulting product hydrolyzed (Wagner and Saizew, *loc. cit.*).

*b.* Action of ethyl magnesium iodide on ethyl formate and hydrolysis of the resultant product (Grignard, *Compt. rend.*, 132, 336 (1901)).

*c.* By reduction of the corresponding ketone (Sabatier and Senderens, *Compt. rend.*, 137, 302 (1903)) and Ponzio (*Gazz. Chim. Ital.*, 31, 404 (1901)).

*Preparation.*—The compound is most readily prepared by Grignard's reaction. See *b* under formation.

*Occurrence.*—Diethyl carbinol has not yet been found in either the animal or vegetable kingdom.

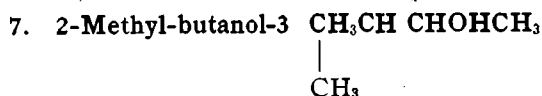
*Identification.*—Oxidation of the alcohol with  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$  forms diethyl ketone, propyl methyl ketone, propionic and acetic acids (Wagner and Saizew, *loc. cit.*). The ketone forms an oxime boiling at 162° C. (Scholl, *Ber.*, 21, 509 (1888)). The semicarbazone prepared from the ketone melts at 139° C. (Mannich and Zernik, *Arch. Pharm.*, 246, 180 (1904)).

The phenyl urethane has been prepared by Mannich and Zernik. They report a melting point of 48–49° C. but repeated attempts to confirm this give liquid products only.

The  $\alpha$ -naphthyl urethane has been prepared by Neuberg and Kansky (*Biochem. Z.*, 20, 445 (1909)). Melting point is 76–79° C. The melting point found from a preparation of Eastman's diethyl carbinol is 61–62° (see chapter on  $\alpha$ -naphthyl urethanes).

The 3,5-dinitro-benzoate melts at 58° C. (see chapter on the 3,5-dinitro-benzoates).

The 3-nitro-acid-phthalate melts at 91° C. (see chapter on 3-nitro-acid-phthalates).



*Synonyms.*—Methyl-isopropyl-carbinol

Secondary isoamyl alcohol

*History.*—While this alcohol was predicted by Kolbe in 1856, it was not until Münch's synthesis in 1875 that this was accomplished (Münch, *Ann.*, 180, 339 (1876)). The first report in which this alcohol was mentioned dealt with the forma-



tion of the ketone, but in order to prove the constitution of this body, reduction was effected.

The alcohol contains an asymmetric carbon atom, but no investigations at attempted separations are reported in the literature. When speaking of optically active amyl alcohol, reference is made to methyl-3-butanol-1 already described.

*Formation.*—*a.* Reduction of methyl-2-butanone-3 with sodium amalgam (Münich, *Ann.*, 180, 339 (1876)).

*b.* Reaction of nitrous acid on 2-methyl-3-amino butane (Trasciatti, *Gazz. Chim. Ital.* 29, 98 (1899)).

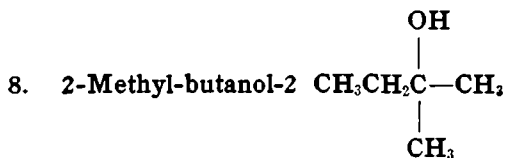
*c.* Action of methyl magnesium bromide on monochloro acetylchloride (Henry, *Compt. rend.*, 145, 24 (1907)).

*d.* Action of methyl magnesium bromide on dichloroacetone (Henry, *Loc. cit.*).

*Occurrence.*—This alcohol has not been found in either the animal or vegetable kingdom.

*Identification.*—Being a secondary alcohol, the body on oxidation should yield the corresponding ketone, which might then be identified either in the form of its oxime, semicarbazone or suitable hydrazone. But oxidation does not stop at the corresponding ketone. Wischnegradski (*Ann.*, 190, 339 (1878)), found that when 2-methyl-butanol-3 was oxidized with  $K_2Cr_2O_7$  and  $H_2SO_4$  the following bodies were obtained: Carbon dioxide, acetic acid, acetone and 2-methyl-butanone-3. The ketone forms a liquid oxime of b. p. 157–158° (Nageli, *Ber.*, 16, 2984 (1883)). The semicarbazone melts at 110° C. (Trasciatti, *Gazz. Chim. Ital.*, 29, 2, 100 (1899)).

Other solid derivatives such as the phenyl and  $\alpha$ -naphthyl urethanes, 3,5-dinitro-benzoate and 3-nitro-acid-phthalate are not described in the literature.



*Synonyms.*—Dimethyl-ethyl-carbinol  
Tertiary-amyl-alcohol  
Amylene-hydrate  
Amylum-hydratum

*History.*—The alcohol was first prepared by Papow in 1868 (*Ann.*, 145, 292). It has come into therapeutic use because of its sedative properties, for which relatively large quantities are being made.

*Formation.*—*a.* Action of zinc dimethyl on propionyl chloride (*Ann.*, 145, 292 (1868)).

*b.* Action of  $ZnCl_2$  on amylenes (*Bull. soc. chim.* (3), 7, 577 (1892)).

*c.* Action of methyl magnesium bromide on diethylidene oxide (Henry, *Compt. rend.*, 145, 406 (1907)).

*d.* Action of  $AgNO_2$  on dimethyl 2,2-amino-3-propane (Freunde and Lenze, *Ber.*, 24, 2519 (1891)).

*Preparation.*—The alcohol may be obtained in 76–79% yields by hydrating amylenes in the presence of  $H_2SO_4$  (Adams, Kamm and Marvel, *Illinois Univ. Bull.*, 16 (June 23, 1919)).

*Occurrence.*—This alcohol has not yet been found in either the animal or vegetable kingdom.

The velocity of esterification with trichloroacetic acid has been studied by Michael and Wolgast (*Ber.*, 42, 3167 (1909)).

*Identification.*—Tertiary alcohols on oxidation decompose to yield compounds with a lesser number of carbon atoms. Tertiary amyl alcohol when oxidized with  $K_2Cr_2O_7$  and  $H_2SO_4$  yields acetone and acetic acid (Wischnegradski, *Ann.*, 190, 335 (1878)).

The solid derivatives which may be used for the identification of this alcohol are here listed.

The phenyl urethane melts at  $42^\circ C.$  (Jambling, *Bull. de Soc. Chim.* (3), 19, 777 (1898)). A redetermination gives  $45^\circ$  as the melting point (see chapter on phenyl urethanes).

The  $\alpha$ -naphthyl urethanes melt at  $71-72^\circ$  (Neuberg and Kansky, *Biochem. Z.*, 20, 445 (1909)).

The 3,5-dinitrobenzoate melts at  $91^\circ C.$  (see chapter on 3,5-dinitrobenzoates).

The 3-nitro-acid phthalate has not yet been prepared. Attempts to prepare the ester result in the decomposition of the tertiary alcohol, and formation of 3-nitro-phthalic acid.

(To be continued)

#### A HOSPITAL INFLUENZA RESEARCH DEPARTMENT.

The Research Department of St. George's Hospital, Hyde Park, London, is making arrangements to inaugurate a special department for the study of the aetiology of influenza, its incidence and methods of prevention. The research work is to begin at once, so that material and evidence can be collected from the current epidemic. One of the earliest efforts will be directed towards the discovery of the causation of influenza, which has not been definitely made, notwithstanding the theories on the subject. Laboratory accommodation has been provided at the hospital for the new department, the cost of which is likely to run to more than £2000 a year.

#### WEIGHTS AND MEASURE LAWS ARE COMPILED.

The Bureau of Standards has announced the forthcoming publication of a new compilation of the weights and measures laws of the Federal, State and territorial governments, and has requested that all who wish copies communicate at once making their requests, as it is intended to print only one edition to fill the requirements indicated.

#### FIRST AID WEEK PUBLICITY.

Retail pharmacists have strongly approved the fine publicity work for pharmacy which many wholesale druggists and manufacturers have put over. At the recent meetings of pharmacists of Minnesota and Iowa, retailers extended thanks for what has been done along this line and urged more similar publicity.

The interest shown during the past month evidences what may be done by coöperation among all divisions of the drug trade.

#### VITAMIN D.

Scientists here and in Europe, working in more or less collaboration on the problem, have come to the same conclusion, according to Dr. Alfred F. Hess, of the College of Physicians and Surgeons at Columbia University, that the anti-rachitic vitamin D is formed when certain sterols are exposed to ultraviolet light. Dr. Hess and Drs. O. Rosenheim and T. A. Webster, of the National Institute for Medical Research in London, have collaborated with Professor A. Windaus, of Göttingen University, in Germany, who has been engaged in research on the chemical problems involved in the isolation of the anti-rachitic vitamin for several years.