UNITED STATES PATENT OFFICE.

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ALCOHOL AND PROCESS OF OBTAINING THE SAME FROM CARBOXYLIC COMPOUNDS.

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To all whom it may concern:

Be it known that we, LOUIS BOUVEAULT and GUSTAVE BLANC, citizens of the Republic of France, residing in Paris, have invented a new and useful Process for the Transformation of the Carboxylic Group CO_2H into the Alcoholic Group CH_2OH, which process is fully set forth in the following specification.

The object of our invention is the preparation of primary alcohols by a process consisting essentially in transforming amido and ether derivatives of the carboxylic groups existing in certain organic molecules into groups— CH_2OH characteristic of alcohols.

Our process of preparation of this class of alcohols permits of obtaining them directly in a state of purity and of preparing in large quantities certain alcohols which have heretofore only been able to be prepared in small quantities.

The general method hitherto used for preparing primary alcohols are not practically applicable either because of the insufficiency of the yield or because of the rarity or high cost of the parent materials.

We have discovered a new simple and practical method whereby monohydric and polyhydric alcohols may be produced in a regular manner and with very satisfactory yield.

This method consists essentially in transforming the carboxylic grouping CO_2H into the alcoholic grouping— CH_2OH by treating the amido and ether derivatives of the acids by sodium and absolute alcohol:

$$\left.\begin{array}{l} \ldots CO.OR \longrightarrow CH_2OH \\ \ldots CO.NH_2 \longrightarrow CH_2OH \\ \ldots CONRR_1 \longrightarrow CH_2.OH \end{array}\right\} \begin{array}{l} R \text{ and } R_1 \text{ being al-} \\ \text{coholic radicals as} \\ \text{methyl, ethyl } \ldots . \end{array}$$

A transformation from acid to alcohol has already been effected by reduction of the chlorids or anhydrids of the acids by sodium amalgam or by the copper-zinc couple, or by reduction of the lactones by sodium amalgam, but the yields are generally poor and the alcohol obtained is always mixed with intermediate products, such as the aldehyde and ester.

The novelty of our method resides in the fact that the esters and the amids whose tendency to suffer reduction in this way had not been suspected hitherto, are reduced to corresponding alcohols by sodium in presence of absolute alcohol; the conditions of the reaction may be varied according to the case in point, and the example hereinafter given should be regarded as a mode of operation and not as a type to be rigorously followed.

The presence of small quantities of water has a disastrous effect on the yield, probably because a part of the ester is then saponified and escapes reduction; for this reason it is of the utmost importance, in order to obtain satisfactory yields to use perfectly absolute alcohol and esters deprived of every trace of moisture.

The following example is given as an instance of the mode of operation which may be adopted in most cases. Into a vessel connected at the top both with a powerful reflux condenser and a dropping funnel there are introduced 6 atomic proportions of sodium in large pieces; there is then run in from the funnel one molecular proportion of the ester or the amid of the acid to be reduced mixed with $\frac{3}{4}$ times its weight of absolute ethyl alcohol or a homologue thereof. The rate of flow into the vessel is regulated so that there may be an energetic reaction without overtaxing the condenser. When all the liquid has been added the reaction is completed by heating for several hours by means of a water-bath or a bath of calcium chlorid; if at this moment the sodium has not completely disappeared a little more alcohol is added. Finally, the whole is allowed to cool and a little water or dilute alcohol derived from a former operation is added and the mixture is distilled to recover the major portion of the ethyl alcohol which is ultimately converted into absolute alcohol. This ethyl alcohol sometimes carries over the alcohol sought and must then be rigorously fractionated. The alkaline liquid left in the vessel contains the original acid in the form of a sodium salt and the alcohol corresponding with this acid. To isolate this alcohol it may be distilled over in steam. At the same time, if the alcohol is sufficiently soluble in water or in soda, the liquid may be neutralized exactly and extracted with a suitable solvent.

To show the broad possibilities of our new invention we give in the following a list of the chemical bodies prepared by our new process. These belong as well to the aliphatic, as to the aromatic and hydrocyclic series; mono- and polyhydric alcohols, saturated and insaturated compounds can be obtained with the same facilities. The new compounds on the list are marked specially.

Alcohols of the Fatty Series.

I. Saturated Alcohols.

By reducing	Alcohols	Boiling point	Density
Ethyl butyrate	Butanol 1	116° (Phényl-urethan[f] 57°)	0.823/0°
Ethyl valerate	Pentanol 1	138-139°	0.829/0°
Ethyl n. caproate or caproic amid	Hexanol 1	156°	0.833 0°
Etyhl isocaproate or ethyl isobutyl-acetoacétate	Methyl$_4$ pentanol$_1$	160-165°	0.836 at 0°
Ethyl methylpropyl aceto acetate	Methyl$_2$ pentanol$_1$	146-148°	0.837 at 0°
Ethyl octanoate	Octanol 1	96° at 15 mm (phenylurethan f[d] 94)	0.838/0°
	+Methyloctyl-oxyd	75° at 20 mm.	
	Octyl acetate	98° at 15 mm.	
	Octyl butyrate	242-244	
	Octyl valerate	250-251	
Ethyl nonylate or nonylamid	Nonanol 1	211-212°	0.842/0°
	+Formate	100° at 10 mm.	
	Acetate	100 at 8 mm.	
	+Butyrate	134-137° at 14 mm.	
	+Valerate	142-146° at 12 mm.	
Ethyl decanoate	Decanol 1	120° at 12 mm.	Melts +8°
Ethyl dimethyl 3.7 Octeneoate	+3.7 dimethyl-octanol 1	115-126 at 15 mm.	0.849/0°
Ethyl β. β. hexyl-methyl acrylate	+Methyl$_2$ nonanol 1	111-116 at 14 mm.	0.856 at 0°
Ethyl laurate	Dodecanol 1	255-259°	Melts +24/
	Acetate	Acetate 140° at 10 mm.	
	+Butyrate	162-164 at 10 mm.	
	+Valerate	170° at 10 mm.	
Ethyl myristate	Tetradecanol 1	160° at 10 mm.	Melts +38

II. Insaturated Alcohols.

By reducing	Alcohols	Boiling point	Density
Ethyl allyl acetate	Pentène 4 ol 1	142°	0.863 at 0°
Ethyl dimethyl 3.7 Octene$_6$oate$_1$	+Dimethyl$_{3.7}$ Octen$_6$ol$_1$	108-112° at 10 mm.	0.877 at 0°
Ethyl undecylenate	+Undecylen 10 ol$_1$	150-152° at 30 mm.	
Ethyl citryliden-acetate	+Dimethyl$_{4.8}$ decadien 4.8 ol 1	150-155° at 17 mm.	
Ethyl citryliden acetate a/	+Alcohol a	150-155° at 15 mm.	
Ethyl citryliden acetylacetate b/	+Alcohol b	170-175° at 20 mm.	
Ethyl oleate	Oleic alcohol	207° at 13 mm.	0.862 at 0°
Ethyl α and β cyclocitrylidenacetate	Cyclo-citryliden ethanol	138-145° at 16 mm.	0.935 at 20°

III. Hydrocyclic and Terpenic Alcohols.

By reducing	Alcohols	Boiling point	Density
Ethyl hexahydrobenzoate	+Hexahydrobenzylalcohol	82° at 11 mm. Phenylurethane Mp. 82°	0.946 at 0°
Ethyl campholenate	+Campholene alcohol	211-213	1.1593
	+Acetat	135-136 at 21 mm.	
	+Butyrate	257-259°	
	+Oxyde	177-179°	0.9303
Ethyl campholate	+Campholic alcohol	213°	Melts at 60°.

IV. Aromatic Alcohols.

By reducing	Alcohols	Boiling point	Density
Ethyl phenylacetate / Phenylacetamide	Phenyl$_2$ethanol$_1$	214-216° / Phenylurethane melts at 80°	1023 at 15°
	Formate	96-97 at 12	
	Acetate	107-109 at 12	1038 at 15°
	Butyrate	130-132 at 12	
	Valerate	134-138 at 10	
Ethyl phenylpropionate			
Ethyl cinnamate	Phenyl$_3$propanol$_1$	120° at 12 mm.	1007 at 15°
	+Formate	117° at 12 mm.	
	+Acetate	127-128 at 12 mm.	
	+Butyrate	151-155 at 16 mm.	
	+Valerate	159-161° at 18 mm.	
Ethyl p.methoxy-phenyl acetate	+Para methoxyphenyl$_2$ ethanol	264-266°	Melting 22-23
	+Acetate	155-157° at 11	

V. Polyhydric Alcohols.

By reducing	Alcohols	Boiling point	Density
Ethyl α α-Dimethylsuccinate	+2.2 Dimethyl butanediol$_{1.4}$	123° at 10 mm.	
Ethyl α α-Dimethylglutarate	+2.2 Dimethyl-pentanediol$_{1.5}$	130° at 12 mm.	
Methyl adipate	Hexane diol 1.6	151° at 12 mm.	Melts at 40°
Methyl β-methyl-adipate	+2 Methyl hexane diol$_{1.6}$	160-165° at 15 mm.	
Ethyl suberate	+Octane diol 1.8	172° at 20 mm.	Melts at 63°
Ethyl sebacate	+Decane diol 1.10	179° at 11 mm.	Melts at 71°5

The alcohols above described obtained by our method are industrially applicable because they can be used either directly or as esters in perfumery, confectionery, distilleries, and like industries, or as parent materials for the preparation of compounds (aldehydes, halogen derivatives or the like) concerned in diverse industries. These examples show the scope of our process and the applications to which it can be applied.

Our method permits the formation of the two following alcohols which are of similar structure and which we claim specially: the 3.7 dimethyl octanol 1 and the 3.7 dimethyl 6 octenol 1. These alcohols are practically obtained by condensation of synthetic methyl 6 heptanone 2 or natural methyl 6 heptenone 2 with ethyliodacetat, by elimination of H_2O, in the thus-formed ether of oxy acid and finally by reduction of the ether of unsaturated acid by sodium and absolute alcohol. These alcohols, which are particularly useful in perfumery, have the following characteristics:—Alcohol 3.7 dimethyl octanol 1 is a colorless liquid at ordinary temperatures, and has a boiling point of 115 to 120 degrees C. at 15 millimeters pressure, a specific gravity of 0.852 at 18 degrees C.; and a refraction index of 1.4401 for the line D. Its pyruvic ester boils at 145 to 150 degrees C. at 15 to 16 millimeters pressure, and gives a semi-carbazone melting at 124 degrees C. Alcohol 3.7 dimethyl 6 octenol 1 is a colorless liquid at ordinary temperatures, and has a boiling point of 108 to 112 degrees C. at 10 millimeters pressure, a spe-

cific gravity of 0.858 at 19 degrees C., and a specific gravity of 0.8762 at 0. degrees C., and has a refraction index of 1.4506 for the D line. Its pyruvic ester boils at 143 degrees C. at 10 millimeters pressure, and gives a semi-carbazone melting at 112 degrees C. Although we have herein claimed specifically the alcohol 3.7 dimethyl octanol 1, it is to be understood that we regard as included in our invention, alcohol 3.7 dimethyl 6 octenol 1.

What we claim is:—

1. The process of transforming a carboxylic group into an alcoholic group, consisting in subjecting a herein described ether derivative of said carboxylic group to the simultaneous action of an alkali metal and absolute alcohol.

2. As an article of manufacture, the alcohol 3.7 dimethyl octanol, being a colorless liquid at ordinary temperatures, and having a boiling point of 115 to 120 degrees C. at 15 millimeters pressure, having a specific gravity of 0.852 at 18 degrees C., having a refraction index of 1.4401 for the D line, and forming a pyruvic ester boiling at 145 to 150 degrees C. at 15 to 16 millimeters pressure, and forming a semi-carbazone melting at 124 degrees C.

In witness whereof we have hereunto signed our names this 12th day of January 1904, in the presence of two subscribing witnesses.

LOUIS BOUVEAULT.
GUSTAVE BLANC.

Witnesses:
JULES ARMENGAUD, Jeune.,
HANSON C. COXE.