

UNITED STATES PATENT OFFICE.

LOUIS BOUVEAULT AND GUSTAVE BLANC, OF PARIS, FRANCE.

ALCOHOL AND PROCESS OF OBTAINING THE SAME FROM CARBOXYLIC COMPOUNDS.

No. 868,252.

Specification of Letters Patent.

Patented Oct. 15, 1907.

Application filed January 23, 1904. Serial No. 190,347.

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.

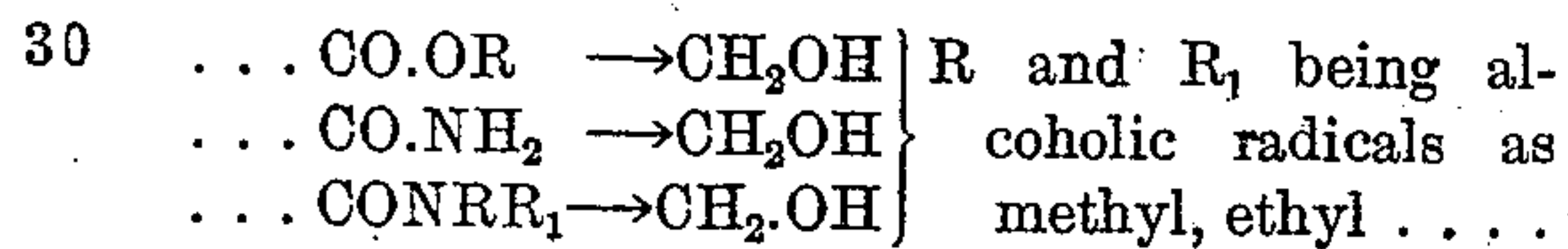
The object of our invention is the preparation of primary alcohols by a process consisting essentially in transforming amido and ether derivatives of the carboxylic groups existing in certain organic molecules into groups— CH_2OH characteristic of alcohols.

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:



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 $\frac{1}{2}$ 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
5	Ethyl butyrate	Butanol 1.....	116° (Phénylurethane 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°
10	Ethyl isocaproate or ethyl isobutyl-acetoacetate	Methyl ₄ pentanol	160-165°.....	0.836 at 0°
	Ethyl methylpropyl aceto acetate	Methyl ₂ pentanol	146-148°.....	0.837 at 0°
15	Ethyl octanoate ...	Octanol 1.....	96° at 15 mm (phenylurethane 94)	0.838/0°
		+Methyloctyl-oxyd	75° at 20 mm..	
20		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°
25		+Formate.....	100° at 10 mm.	
		Acetate.....	100 at 8 mm.	
		+Butyrate.....	134-137° at 14 mm.	
		+Valerate.....	142-146° at 12 mm.	
30	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-methylacrylate	+Methyl ₂ nonanol 1	111-116 at 14 mm.	0.856 at 0°
35	Ethyl laurate.....	Dodecanol 1....	255-256°.....	Melts +24/
		Acetate.....	Acetate 140° at 10 mm.	
		+Butyrate.....	162-164 at 10 mm.	
40	Ethyl myristate...	+Valerate.....	170° at 10 mm.	
		Tetradecanol 1.	160° at 10 mm.	Melts +38

II. INSATURATED ALCOHOLS.

	By reducing	Alcohols	Boiling point	Density
45	Ethyl allyl acetate	Pentène 4 ol 1...	142°.....	0.863 at 0°
	Ethyl dimethyl 3.7 Octeneoate	+Dimethyl _{2,7} Octenol	108-112° at 10 mm.	0.877 at 0°
	Ethyl undecylenate	+Undecylen 10 ol	150-152° at 30 mm.	
50	Ethyl citrylidenacetate	+Dimethyl _{2,3} decadien 4.8 ol 1	150-155° at 17 mm.	
	Ethyl citrylidenacetate a/	+Alcohol a.....	150-155° at 15 mm.	
55	Ethyl citrylidenacetate 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°

60 III. HYDROCYCLIC AND TERPENIC ALCOHOLS.

	By reducing	Alcohols	Boiling point	Density
65	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.	
70	Ethyl campholate..	+Butyrate.....	257-259°.....	0.9303
		+Oxyde.....	177-179°.....	
		+Campholic alcohol	213°.....	Melts at 60°

IV. AROMATIC ALCOHOLS.

By reducing	Alcohols	Boiling point	Density	
Ethyl phenylacetate Phenylacetamide ..	Phenyl ₂ ethanol	214-216°.....	1023 at 15°	75
	Formate	96-97 at 12....		
	Acetate.....	107-109 at 12..	1038 at 15°	80
	Butyrate.....	130-132 at 12..		
	Valerate.....	134-138 at 10..		
Ethyl phenylpropionate Ethyl cinnamate ..	Phenylpropa-nol	120° at 12 mm.	1007 at 15°	85
	+Formate	117° at 12 mm.		
	+Acetate.....	127-128 at 12 mm.		90
	+Butyrate.....	151-155 at 16 mm.		
	+Valerate.....	159-161° at 18 mm.		
Ethyl p-methoxyphenylacetate	+Para methoxyphenyl ethanol	264-266°.....	Melting 22-23	95
	+Acetate.....	155-157° at 11		

V. POLYHYDRIC ALCOHOLS.

By reducing	Alcohols	Boiling point	Density	
Ethyl α α-Dimethylsuccinate	+2.2 Dimethyl butanediol ₄	123° at 10 mm.		100
Ethyl α α-Dimethylglutarate	+2.2 Dimethyl-pentanediol ₅	130° at 12 mm.		
Methyl adipate	Hexane diol 1.6	151° at 12 mm.	Melts at 40°	105
Methyl β-methyladipate	+2 Methyl hexane diol ₆	160-165° at 15 mm.		
Ethyl suberate	+Octane diol 1.8	172° at 20 mm.	Melts at 63°	110
Ethylsebacate.....	+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 H₂O, 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 5 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.

10 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 15 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 20 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 25 subscribing witnesses.

LOUIS BOUVEAULT.
GUSTAVE BLANC.

Witnesses:

JULES ARMENGAUD, Jeune.,
HANSON C. COXE.