

UNITED STATES PATENT OFFICE.

CHARLES METTLER, OF MUNICH, GERMANY.

PROCESS OF PRODUCING AROMATIC ALCOHOLS AND THEIR DERIVATIVES.

No. 815,548.

Specification of Letters Patent.

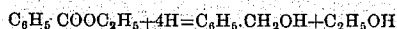
Patented March 20, 1906.

Application filed November 2, 1904. Serial No. 231,149.

To all whom it may concern:

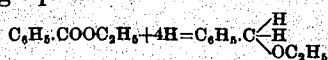
Be it known that I, CHARLES METTLER, chemist, a citizen of Switzerland, of No. 12 Marsstrasse, Munich, in the Kingdom of Bavaria and Empire of Germany, have invented certain new and useful Improvements in Processes for the Production of Aromatic Alcohols and their Derivatives, of which the following is a specification.

It has not hitherto been known that a reduction of aromatic esters to alcohols, for example, from ethyl-ester of benzoic acid to benzylalcohol



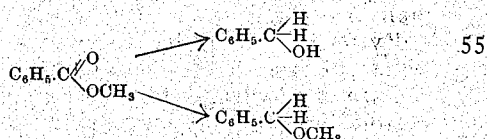
has ever been realized.

I have now found that aromatic esters have the property, under the conditions suitable for the same, of taking up hydrogen and changing into compounds comparatively poor in oxygen. This occurs when aromatic esters are reduced at metal cathodes—for example, at lead cathodes—by means of electrolytically-separated hydrogen. For this purpose it is advantageous to employ a dissolving agent for the ester, which is at the same time capable of conducting the electric current, as such comes into consideration, concentrated sulfuric acid which can be diluted with water, alcohol, or acetic acid. In lieu thereof an aqueous alcoholic solution of hydrochloric acid can be employed, and finally such a reduction can also be carried out in an alkaline or neutral solution, in which case an aqueous solution which contains the electrolyte is mixed with the quantity of alcohol necessary for the solution of the ester. If one operates in an acid solution and reduces by way of example ethyl ester of benzoic acid after a sufficient time that the current has passed all ester has disappeared, and in its place in approximately quantitative yield a new reaction product is obtained which partially consists of benzyl alcohol, besides which another compound results—namely, a derivative of benzyl alcohol, benzylethylether of a boiling-point of 185° centigrade, which is formed according to the following equation:

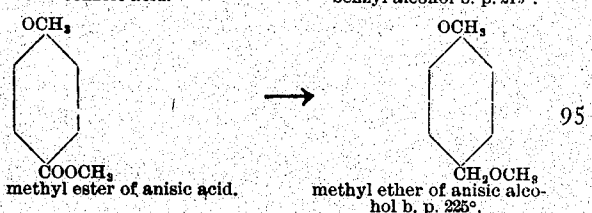
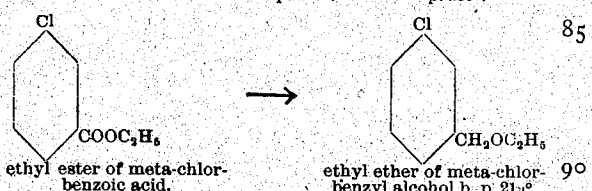
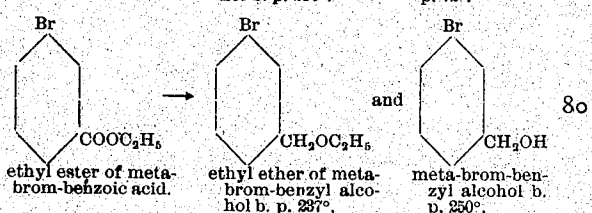
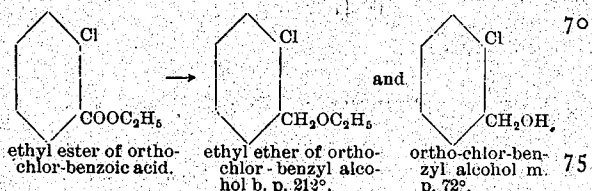


In a similar manner benzylalcohol and ben-

zylmethylether (boiling-point 168°) are formed out of methyl ester of benzoic acid



This course of reactions is not only limited to the various ethyl esters of benzoic acid; but it relates to a new general class reaction of aromatic esters. It is particularly of value in that it also holds good for substituted aromatic esters. Thus when using halogen-substituted esters of benzoic acid the halogen is not replaced by hydrogen, but the latter acts exclusively, reducing on the carboxyl group. Thus one obtains:



With regard to the proportions of ether and of alcohol, these depend upon quite a number of circumstances. For example, con-

stitution and temperature play an important part. If the methyl ester of benzoic acid is treated, the production of alcohol prevails formed, (two parts alcohol, one part ether,) whereas out of ethyl ester of benzoic acid under analogous conditions more ether is formed (one part alcohol, two parts ether.) The formation of ether is still more predominant in the case of the halogen-substituted compounds. Thus, for example, the ethyl ester of meta-chlor-benzoic acid is exclusively reduced to ethyl ether of meta-chlor-benzyl alcohol. The reduction of the esters can also be carried out in an alkaline solution. As main products alcohols are obtained.

By means of suitable oxidizing agents the ethers, like the alcohols, can easily be converted into aldehydes, and these form a suitable material for the dyeing industry for tri-phenyl-methan dyestuffs and for artificial indigo.

The following examples will now be given:

1. The cathode-space of an electrolyzing apparatus is charged with a solution having the following composition: three hundred grams of ethyl ester of benzoic acid, three hundred and fifty grams of concentrated sulfuric acid, five hundred grams of alcohol of ninety-six per cent., one hundred grams of water. (In place of water a correspondingly dilute solution of sulfuric acid can of course be employed.) The anode-space separated by an earthenware cell contains sulfuric acid diluted with water. It is known that the electrolytic reduction of substances which are not readily and easily reduced can be facilitated by employing for the cathode a metal having a high cathodic tension. Therefore the cathode of my apparatus consists of pure sheet-lead, which is suitably prepared according to Tafel's prescription, (*Berichte der Deutschen Chem. Gesellschaft* 33.2215,) and pure lead is employed for the anode. A current of seven amperes per one hundred square centimeters cathode-surface is sent through the liquid; but the strength of the current can be materially varied without disadvantage. By means of cooling the temperature is kept between 20° and 30° centigrade. When no more hydrogen is absorbed, the cathode liquid is neutralized with about thirty per cent. soda-lye. Two layers are formed, of which the upper one consists of al-

cohol and the products of reduction of the ethylester of benzoic acid. This is separated, distilled, and fractionized. The benzyl-ethyl ether boils at 184°, the benzyl alcohol at 205°.

2. Under similar conditions as in Case 1 a cathode liquid of the following composition—namely, one hundred and seventy grams of ethyl ester of meta-brom-benzoic acid, three hundred grams of concentrated sulfuric acid, five hundred grams of alcohol of ninety-six per cent.—is reduced at a lead cathode with the aid of the electric current. During the electrolysis the reaction product is separated for the greater part on the bottom of the cathode-space as oil. It is drawn off and distilled. Between 235° to 239° the ethyl ether of meta-brom-benzyl alcohol distills. At 250° a small quantity of meta-brom-benzyl alcohol passes over.

3. In the cathode-space of an electrolyzing apparatus a solution as follows is placed: one hundred grams of ethyl ester of benzoic acid, six hundred grams of thirty-per-cent. aqueous sal-ammoniac solution, six hundred grams of alcohol. The anode-space separated by an earthenware cell contains dilute sulfuric acid or ammonium-sulfate solution. Cathode and anode consist of pure lead. Electrolysis proceeds while the liquid is cooled, the current having a strength of six amperes per one hundred square centimeters cathode-surface. When no more hydrogen is absorbed, the alcohol is distilled off and the liquid is acidulated. Benzyl alcohol separates for the most part. It is removed and distilled. (195° to 205°.)

What I claim is—

Process for the production of aromatic alcohols and their ethers, which consists in exposing the aromatic esters in a dissolving agent, capable of conducting the electric current in the cathode-space of an electrolytic apparatus in using for the cathode a material of a specially-high cathodic tension, then neutralizing the cathode liquid, then separating the reaction product and finally distilling, substantially as described.

In witness whereof I have hereunto set my hand in the presence of two witnesses.

CHARLES METTLER.

Witnesses:

ULYSSES J. BYWATER,
ABRAHAM SCHLESINGER.