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PROCESS FOR MANUFACTURING CARBINOLS HAVING AN ACETYLENIC FUNCTION

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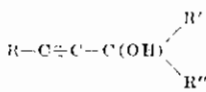
It is known that carbinols with an acetylene function can be obtained by the action of substances possessing a carbonyl group =C=O, either on the acetylides of alkali metals, or on organo-metallic derivatives of acetylene or substitution products of the latter.

The first method offers serious drawbacks for carrying it out industrially, since it requires very low temperatures, of the order of —30° to —40° C., solvents such as liquid ammonia, and the use of expensive products such as metallic sodium or sodium amide.

The second method, that is to say the preparation by means of organo-metallic substances, is practically inapplicable industrially.

It has also been proposed to obtain acetylene carbinols, such as phenylacetylene derivatives, by reacting the latter with acetone in the presence of powdered potash, the products resulting from this reaction being carbinols of the general formula:



It has also been proposed to replace the substitution products of acetylene by acetylene itself. This reaction was effected in the presence of ethyl ether as a solvent. But this solvent has serious drawbacks from the industrial standpoint, owing to its volatility, its inflammability and the dangers of explosion that may be caused by the formation of peroxides. This danger may be increased, in the applications in question, since said peroxides may react with the acetylene compounds formed and produce substances which are particularly explosive.

We have found, and this is what the invention consists in, that the reaction of acetylene or mono-substituted acetylene with products containing a carbonyl group, in the presence of solid potash, for forming acetylene carbinols, can be effected in certain solvents, other than ethyl ether, which do not have the serious drawbacks of the latter.

The solvents which enable the reaction in question to be effected must contain atoms such as trivalent nitrogen, bivalent oxygen, or other atoms capable of changing to a higher valency. Such solvents may, for example, be ether-oxides, acetals, tertiary amines, etc.

In order that the reaction shall take place under satisfactory conditions and with maximum efficiency, it is preferable to mix the potash beforehand with the above mentioned active solvents, at a suitable temperature which depends on the nature of the solvent. I have found that this method of proceeding favours the subsequent formation of the potassium derivative.

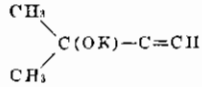
It is advisable to form a certain quantity of this potassium derivative by introducing a part of the acetylene substance before beginning to introduce the substance containing a carbonyl group it is desired to combine therewith.

We then continue to introduce the substance having an acetylene function, so as to keep the whole or a part of the initially formed quantity of potassium derivative in the reaction mixture.

Example 1

175 parts of powdered potash are mixed with 250 parts of dimethylformal, performing the function of an active solvent, at a temperature of about 15° C., and the temperature is allowed to rise to about 30–35° C. The mixture is cooled to about 0° C., then about 10 parts of acetylene are introduced. Then 60 parts of acetone are gradually added and 23 further parts of acetylene.

The potassium derivative of the corresponding acetylene carbinol is formed:



Decomposition is effected with water and, after the evolution of the excess of acetylene and the separation of the aqueous layer, the solvent is separated from the carbinol formed, by distillation.

About 80 parts of carbinol are obtained, whereof the boiling point is 104–106° C.

Example 2

450 parts of diethylaniline are mixed with 175 parts of powdered potash. After introducing 4 parts of acetylene into this mixture, 60 parts of acetone are added, and the introduction of the acetylene is simultaneously continued. After adding 16 parts of acetylene, the reaction product is decomposed with water and the operation is continued as in the previous example.

Example 3

175 parts of powdered potash are mixed with 500 parts of dimethylformal, at a temperature of about 15° C. and the temperature is allowed to rise to about 30–35° C. The mixture is cooled to about 0° C., then about 20 parts of acetylene are introduced. 45 parts of acetaldehyde in solution in 100 parts of dimethyformal are then grad-

ually added, and the introduction of acetylene is simultaneously continued. After adding 10 parts of acetylene, the reaction product is decomposed with water, and the operation is continued as in example 1.

Methyl-acetyleneyl-carbinol having the formula:

$$CH_3—CH(OH)—C\equiv CH$$

is thus obtained, whereof the boiling point is 103–105° C.

Of course, the examples given are purely explanatory and in no way limitative, and it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is therefore aimed in the appended claims to cover all such changes and modifications as fall within the true spirit and scope of the invention.

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