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PRODUCTION OF ETHYLENE HYDROCARBONS

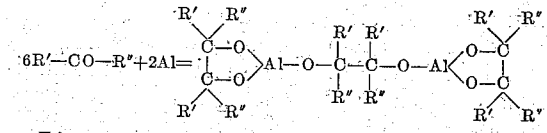
No Drawing. Original application filed May 18, 1926, Serial No. 109,961, now Patent No. 1,752,016, dated March 25, 1930. Divided and this application filed October 16, 1929. Serial No. 400,165.

This case is a division of my application Serial No. 109,961, filed May 18, 1926, now Patent No. 1,752,016, issued March 25, 1930.

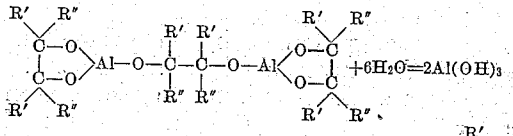
The present invention relates to the production of homologues of ethylene gylcol and ethylene hydrocarbons, and to the production of pinacone from acetone. More particularly the invention relates to the activation of an aluminum reagent by the formation of a thin layer of an active amalgam upon the surface of the aluminum.

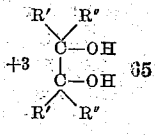
The ordinary method of amalgamating aluminum for use in the reduction of organic compounds does not impart to it sufficient activity. According to the present invention the introduction of a third metal into the amalgam greatly increases the activity thereof and at the same time permits carrying out reactions which are impossible with aluminum activated by the usual methods. The metal introduced into the ordinary aluminum-mercury amalgam is preferably zinc. Other metals, such as cadmium may also be employed. While the invention is not limited to any particular method of forming the reagent, the following may serve as illustrations.

The amalgam may be conducted by the use of soluble salts of mercury and of the third metal, these salts being precipitated upon aluminum which is immersed or suspended in the solution of these salts. Another method of forming the amalgam of this invention is to melt the aluminum and third metal together thus forming an alloy which may then be ground to any desired degree and subsequently amalgamated on its surface by treatment with the mercury salts. When acetone and other ketones and derivatives thereof are treated with the improved reagent it will be found that the nature of the reaction is dependent upon the amount of third metal present in the amalgam. When ketones are treated with aluminum, upon which is deposited an aluminum-mercury-zinc amalgam containing 1 to 2% of zinc, a direct addition of aluminum to the ketone occurs, with the formation of aluminum glycolates according to the following general reaction:



If the glycolate thus obtained be treated with water, a glycol and aluminum-hydroxide are obtained:





When acetone is treated with the improved reagent the end product will be tetramethyl ethylene glycol or pinacol.

If the amount of third metal be increased to from 7 to 30% by weight of the aluminum, ethylene hydrocarbons are produced when ketones are treated. For example acetone will yield propylene:

$$3CH_3-CO-CH_3+2Al=3CH_2=CH-CH_3+Al_2O_3$$

The above equations describe reactions which take place in a non-aqueous medium. If water be introduced into the reacting mixture, nascent hydrogen is evolved. This nascent hydrogen will lead to the formation of a series of reduction products. Under such conditions ketones will produce secondary alcohols:

$$CH_3-CO-CH_3+2H=CH_3-CH-OH-CH_3$$

The improved activated aluminum reagent may be prepared by amalgamating an alloy of aluminum and another metal, preferably zinc. In this instance the amalgam is prepared according to the standard practice of forming mercury amalgams of metals. Amalgams made with mercury and pure aluminum are subject to the disadvantage that the layer of amalgam is rather easily detached during the reaction and frequently the reaction stops as the result of this. With

zinc present in the amalgam layer a viscous tacky material is formed in which, the zinc may act as a cementing substance to keep the aluminum and mercury together. By increasing the percentage of zinc, say up to 30% in the aluminum zinc alloy, a large percentage of propylene will appear in the reaction when acetone is used as the starting material. When an alloy contains 7% of zinc, propylene continues to appear in large quantities in this reaction. When the amount of zinc is reduced to 2% or less, very little propylene will appear, and pinacone is obtained as the main product.

The same results may be obtained by using mixtures of zinc and mercuric salts with aluminum in the preparation of the amalgam.

For instance if amalgamation of the aluminum is carried out by using a solution of 5% of zinc chloride and 10% mercuric chloride, the treatment of acetone with such amalgamated aluminum yields pinacol in large quantities, and relatively free from propylene and other products.

The advantage gained by the present invention is that any kind of aluminum may be employed, and the aluminum may be used in the form of filings or even in the form of rough shavings. Moreover it has been the experience of organic chemists that not all makes of pure aluminum may be employed in carrying out these catalytic reactions. Indeed it is the general experience that there is but one kind of aluminum a product made in Germany which will yield pinacone as the product of the reduction of acetone. By practicing the present invention, however, any kind of aluminum may be employed and even better results obtained than with the above-mentioned foreign product. The percentage of zinc present in the alloy may be varied within wide limits, depending upon the product desired. For the production of pinacone approximately 3% or less of zinc will give excellent results. If propylene or other ethylene hydrocarbons are desired, a higher amount of zinc, even up to 30%, may be used to advantage, although quantities of the unsaturated hydrocarbon will be obtained with 7% of zinc. It is understood, of course, that the percentage of zinc is figured to metallic zinc. If a zinc compound is employed, calculations are made accordingly. For example zinc chloride will analyze a little less than 50% of zinc as metal. It will thus be seen that the reduction of organic oxygen-containing substances particularly the ketones and other compounds which are ordinarily reduced by nascent hydrogen formed by amalgamated aluminum in the presence of water, can be carried out much more economically and with better results than has hitherto been possible. Furthermore the invention possesses the advantage that any type of aluminum can be employed and that it is not essential to have the aluminum in a very finely divided state. Instead of zinc, cadmium may be employed in the same manner.

The production of ethylene glycols and ethylene hydrocarbons, and the reduction or conversion of ketones and their derivatives serve as illustrations of some of the uses to which the improved aluminum amalgam may be put. It will be understood, however, that the reagent may be variously employed in reduction reactions in the presence of water, as well as in reactions where the aluminum forms a compound with all or part of the reacting material. The claims are therefore to be interpreted broadly. The expressions "metallic element", metal and "zinc" as used in the claims, are descriptive of these materials as single elements, or where they are available as such for the purposes of the invention, and the percentages given in the claims refer to percentages of the metal, not of its salt. It is to be understood therefore that salts of zinc and the other metals which may be employed are comprehended by the claims.

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. In the production of ethylene hydrocarbons from ketones, the step of subjecting said ketones to the action of aluminum amalgam containing another metallic element selected from the group consisting of zinc and cadmium said metallic element being present in the amalgam in excess of 3% and not greater than 30% by weight of the aluminum in the amalgam.

2. In the production of ethylene hydrocarbons from ketones, the step of subjecting said ketones to the action of aluminum amalgam containing another metallic element in excess of 3% selected from the group consisting of zinc and cadimum.

3. In the production of ethylene hydrocarbons from ketones, the step of subjecting said ketones to the action of aluminum amalgam containing zinc in excess of 3%.

4. A method for the production of propylene from acetone, which comprises treating acetone with an aluminum amalgam containing more than approximately 3% of zinc.

Signed at Turin, Italy, this 25th day of September, 1929.

ALEXANDER T. MAXIMOFF.