

ALIEN PROPERTY CUSTODIAN

METHOD FOR PREPARING CONDENSATION PRODUCTS OF THE TYPE OF THE FURYL-METHANE DERIVATIVES

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No Drawing. Application filed November 28, 1939

This invention relates to a method for preparing condensation products of the type of the furylmethane derivatives.

Organic compounds having a hydroxyl or amino group can be condensed with aldehydes, for instance phenols can be condensed with formaldehyde, acetaldehyde, benzaldehyde, furfural and hydroxymethylfurfural, and in many cases the condensation can be satisfactorily carried out in an acid medium. Where compounds of the type of furfural and hydroxymethylfurfural are being treated in an acid medium, however, there is a tendency for non-uniform products to be obtained and for undesirable side reactions to take place. For instance, hydroxymethylfurfural shows a tendency to form laevuline acid and formic acid by opening of the ring and to form complex compounds of the type usually called humus substances.

Furane derivatives can also be formed from carbohydrates by the action for instance of phloroglucinol and hydrochloric acid or resorcinol and hydrochloric acid, according to the method of Seliwanoff or Flehe, and methods of detecting pentoses and hexoses exist based on such reactions, which involve the intermediate production of a furfural body from the carbohydrate. However, it can be seen from *Berichte* 37, 304 (1904), *Zeitschrift für Analytische Chemie* 66, 134-7, *Cellulose Chemie* 6, 61 and 81 (1925), and the textbook "Chemie der Zellulose" by K. Hess that the normal condensation product of hydroxymethylfurfural with for instance phloroglucinol is only partly soluble in alcohol and is not a homogeneous substance. This is true whether the hydroxymethylfurfural is formed from a sugar in the reaction or is a pure substance previously prepared, and it seems that the hydroxymethylfurfural is partly decomposed in side reactions, leading, for instance to the formation of humus substances.

This invention is concerned with a method of producing, from carbohydrates and organic compounds (especially aromatic compounds) having one or more free or substituted hydroxyl or amino groups, good yields of relatively homogeneous condensation products.

It has now been found that when forming condensation products of the furylmethane derivative type in this way in the presence of an acid, improved results are obtained if the reaction is carried out in the presence of such a quantity of the said organic compound that an excess of this compound relative to the furfural body is present throughout the reaction.

As indicated above, the first stage of the reaction consists in the formation of a furfural body from the carbo-hydrate, this furfural body then condensing with the organic compound having one or more free or substituted hydroxy or amino groups (which compound may be introduced as such or in solution) and the rate of formation of the furfural body in the first stage of the process depends upon such considerations as the temperature and the quantity of acid used and its nature. The higher the temperature and the greater the quantity of acid the faster is the furfural body formed. Suitable acids are the mineral acids, including sulphuric acid, hydrochloric acid and phosphoric acid, and strong organic acids, e. g. phenol sulphonic acid. Acid compounds such as phosphorous oxychloride (POCl₃) are suitable, and are included in the term "acid" in the preceding paragraph. Mixtures of acids can be used.

In order to obtain as high a yield of the furylmethane derivative as possible care should be taken that there is no local formation of too much of the furfural body relative to the organic compound with which it is to be condensed, which would reduce the excess of this organic compound locally, and hence homogeneous conditions throughout the reaction mixture are desirable. There is then little loss of the furfural body by undesirable side-reactions.

One way of ensuring that the required excess of the organic compound containing one or more free or substituted hydroxy or amino groups is always present is to introduce at the beginning of the reaction so much of the organic compound that an adequate quantity of it remains at the end of the reaction. Another way is to carry out the reaction in such a manner that the relative proportions of the furfural body and the said organic compound present in the reaction mixture remain approximately the same as the reaction proceeds, this proportion being such that the desired excess of the aromatic compound is present. The rate at which the furfural body is formed depends upon the ratio of the acid to the carbohydrate, and in the second of the above two cases the amount of the organic compound present with which the furfural body is to be condensed therefore depends upon this ratio.

Examples of carbohydrates which may be used are sucrose, glucose, mannose, dextrine and starch and mixtures of these, and the hexoses and polyhexoses (i. e. di and polysaccharides containing hexose units) are especially suitable. Other carbohydrates can, however, be employed

provided of course that they can be converted into furfural bodies. It must be remembered that all the carbohydrates do not change to the furfural bodies at the same speed, and this must be taken into consideration in calculating the excess of the organic compound which must always be present during the reaction.

The organic compound containing one or more free or substituted hydroxy or amino groups may, for instance, be an aromatic or hydro-aromatic substance, e. g. phenol, resorcinol, phloroglucinol or dimethylhydroaniline, or may be an aliphatic substance, for instance mannitol or other polyalcohol.

The invention is illustrated by the following examples.

Example 1.—4 gram molecules of resorcinol are dissolved in 25 - 35% hydrochloric acid or 30 - 35% sulphuric acid. 1 gram molecule of fructose or glucose is then added in very finely powdered form to the solution in the cold and is dissolved with continued stirring. The solution is then heated to 50 - 90° C, when a red solid gradually separates. This substance appears to be a diphenyl furylmethane compound formed from two molecules of the resorcinol with one molecule of hydroxymethyl-furfural which has been formed by the action of the acid on the sugar, which seems to be converted almost quantitatively into the diphenylfurylmethane compound. The solid substance is then filtered off and washed.

The product appears to be completely soluble in alcohol or acetone, but not in benzene, and is also soluble in aqueous inorganic bases. It can be converted into a resinous substance of the thermo-setting type by condensing it with formaldehyde in the presence of an alkali or with hexamethylenetetramine. The product can also by careful sulphonation be converted into a water-soluble compound suitable for use as a tanning substance in tanning leather and as colouring means for use with cotton and other materials.

Example 2.—0.5 to 0.75 or 1 gram molecule of concentrated sulphuric acid of specific gravity 1.84 is added to 4 to 8 gram molecules of phenol. The mixture is heated to a temperature between 110 and 170° C with continued stirring and 1 gram molecule of glucose in finely powdered form is gradually added in small quantities. The mixture is then kept for one to two hours at the selected temperature with continued stirring, and the acid concentration indicated above ensures a sufficiently rapid reaction. Water vapour and phenol vapour evolved can be condensed in the usual way. On completion of the reaction the excess of phenol is removed, for instance by extraction with benzene, and the reaction product is washed free from acid by means of water.

The product appears to have been formed in the same way as indicated in Example 1, two

molecules of phenol having condensed with one molecule of hydroxymethylfurfural which has been formed almost quantitatively from the carbo-hydroxide. The product has similar properties to that of Example 1.

Example 3.—A reaction product similar to that of Example 2 can be obtained under conditions similar to those described in Example 2 by adding 1 gram molecule of sucrose to a mixture at least 5 gram molecules of phenol and a quantity of concentrated sulphuric acid, for instance 0.05 to 0.1 gram molecules.

Example 4.—Under reaction conditions similar to those described in Example 2, one gram molecule of very finely powdered fructose is added at a temperature of 110-120° C to 8 gram molecules of phenol and a quantity of sulphuric acid, for instance one third gram molecule.

The purified reaction product has properties similar to those of the products of Examples 1 to 3.

Example 5.—In this example, phenol sulphonic acid previously prepared is used instead of a mixture of phenol and sulphuric acid. Thus the carbohydrate, e. g. glucose or sucrose, can be gradually added in a very finely powdered form to the phenol sulphonic acid at a temperature of 110 to 120° C, or there may be added to the phenol sulphonic acid first a quantity of phenol and then, at 110 to 170° C, the finely powdered carbohydrate, in small quantities.

Example 6.—20 grams of phosphorous oxychloride (POCl₃) are mixed with 100 grams of dimethylaniline and 18 grams of sucrose or glucose in a very finely powdered form are very gradually added to the mixture. On completion of the reaction the acid is neutralized, the excess of dimethylaniline is removed, for instance by steam distillation, and the reaction product is dried.

The product is completely soluble in dilute acids and in alcohols, acetone and other solvents. The product is analogous to the leucobases of malachite green, and by careful oxidation in for example an acid medium can be converted into a dark blue pigment of high colouring power.

Example 7.—Example 6 is repeated, except that 100 grams of dimethylhydroaniline are used instead of the 100 grams of dimethylaniline, and 20 grams of phosgene are used instead of the 20 grams of phosphorous oxychloride.

Example 8.—1 gram molecule of hexose or 0.5 gram molecule of sucrose in finely ground condition is very gradually added to a mixture of 6 gram molecules of mannitol and 0.1 to 0.5 gram molecules of sulphuric acid, at a temperature of 160 - 170° C.

The reaction product is a resinous substance completely soluble in the usual solvents and substantially free from humus substances.

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