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2,763,700

PREPARATION OF SODIUM DERIVATIVES OF WEAKLY ACIDIC HYDROCARBONS

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This invention relates to a process for preparing sodium derivatives of weakly acidic hydrocarbons, and more particularly of hydrocarbons containing the cyclopentadiene nucleus.

The sodium derivatives of hydrocarbons are important intermediates in the formation of a wide variety of organic compounds. Other organo-metallic compounds may be formed by replacing the sodium with a different metal, and condensation products may be obtained by the reaction of the sodium derivatives with organic halides. As described and claimed in my U. S. application Serial No. 312,658, filed October 1, 1952, the sodium derivative of cyclopentadiene has been found to react with iron and nickel halides to form the corresponding dicyclopentadienyl iron and nickel compounds in good yields. These recently-discovered compounds are the first true organo-metallic compounds of iron and nickel which have been prepared. The former is disclosed and claimed in pending U. S. application Serial No. 291,567, filed May 5, 1952, now Patent No. 2,680,756 and the latter in pending U. S. application Serial No. 298,170, filed July 10, 1952, now Patent No. 2,680,758.

Other useful compounds which may be made from the sodium derivatives of hydrocarbons include 9-alkyl fluorenes and fluorene-9-carboxylic acid which result from the treatment with alkyl halides and with carbon dioxide, respectively.

The sodium derivatives of hydrocarbons, however, are difficult to prepare by the methods of the prior art. Such compounds have been made by reacting the hydrocarbon with sodium in ammonia in an autoclave at ordinary temperature for several days, or by reaction with sodium in boiling xylene. Grenshaw et al. in J. Chem. Soc. 51, 2848 (1951) review the various known methods for making 9-fluorenyl sodium, which include the fusion of fluorene at high temperature with sodium or sodamide or refluxing with finely divided sodamide in ether, xylene, or decahydronaphthalene. These methods are relatively slow and result in low yields of the desired product.

It is an object of this invention to provide a method for the preparation of sodium derivatives of weakly acidic hydrocarbons by a reaction which proceeds rapidly and which gives a high yield of the product in a desirable state of purity. A further object is to provide such a process which uses inexpensive reactants and which does not involve the use of elevated temperatures. Further objects will appear from the description which follows.

According to this invention, the sodium derivatives of weakly acidic hydrocarbons containing the cyclopentadiene nucleus are obtained by reacting the said hydrocarbon with sodium acetylide. The reaction is ordinarily carried out in a liquid medium, which must be inert with respect to the reactants, and which is preferably liquid anhydrous ammonia.

The hydrocarbons to which this invention is applicable include cyclopentadiene, its benzo derivatives such as indene and fluorene, and the homologues and phenyl de-

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rivatives of these compounds such as 9-phenyl fluorene, 1-methyl indene, 2-methyl indene, 1-phenyl indene and 2-phenyl indene. In general, the hydrocarbon should be at least as acidic as fluorene in order for the reaction to take place readily. An approximate measure of the acidity of such compounds is afforded by the scale of pKa values given in Hammett, "Physical Organic Chemistry," page 50 (McGraw-Hill, 1940). The pKa value represents the negative logarithm of the ionization constant. Fluorene has a pKa of 25, while indene and 9-phenyl fluorene have pKa values of 21. Any hydrocarbons containing the cyclopentadiene nucleus and having a pKa value of 25 or less are believed to be operable in the process of this invention.

The sodium acetylide taking part in the reaction may be prepared by any of the known methods, the most convenient ordinarily being by the direct reaction of metallic sodium in liquid ammonia with an excess of acetylene. By this method, the sodium acetylide is produced in solution in the liquid ammonia, in a form in which it may be reacted with the hydrocarbon without first having to isolate the acetylide.

The reaction between the hydrocarbon and the sodium acetylide can take place at room temperature or below, as for example, at the boiling point of liquid ammonia. When ammonia is employed as a solvent, the reaction product is conveniently recovered by replacing the ammonia with dry ethyl ether after the reaction is complete and filtering off the precipitated product. Instead of recovering the sodium compound by filtration, it may be reacted directly in suspension form with other materials to form derivatives thereof.

The process of this invention is illustrated by the following examples:

Example 1

Eighty-three (83) grams of fluorene are added to a solution of sodium acetylide, formed from 11.5 grams of sodium and an excess of acetylene, in 450 cc. of anhydrous ammonia. The yellow color of 9-fluorenyl sodium appears immediately. The ammonia is replaced by ether and the ether suspension is filtered. The filtrate contains essentially no fluorene. The filter cake consists of about 90 grams of essentially pure 9-fluorenyl sodium representing a 96% yield. The product contains 12.45% sodium, as compared with the theoretical 12.25%.

When an excess of solid carbon dioxide is added to the ether suspension prior to filtration and the mixture is then filtered, the filter cake consists of the essentially pure sodium derivative of 9-fluorenyl carboxylic acid.

Example 2

A solution of sodium acetylide is prepared by reacting 11.5 grams of sodium and an excess of acetylene in 450 cc. of liquid anhydrous ammonia. To this solution are added 33 grams of freshly distilled cyclopentadiene and the mixture is refluxed at -32° C. with agitation and under a blanket of nitrogen. Cyclopentadienyl sodium precipitates from the liquid ammonia as a somewhat brownish, not obviously crystalline solid which is also insoluble in ether. The ammonia is replaced by dry ethyl ether and the mixture is refluxed at 35° C. for one hour. Twenty-eight (28) grams of ferric chloride are added and the mixture is agitated at room temperature for 16 hours. There results bis-cyclopentadienyl iron in a yield of 44.1%, based on the ferric chloride.

The process of this invention proceeds rapidly to give high yields of the sodium compounds, which in some cases are nearly quantitative. The reaction product is prepared in a form which may conveniently be used directly in the preparation of other organic compounds.

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I claim:

1. A process for the preparation of a sodium derivative of a hydrocarbon containing the cyclopentadiene nucleus and being at least as acidic as fluorene which comprises effecting reaction between the said hydrocarbon and sodium acetylide by bringing the reactants into contact with one another in a liquid medium which is inert with respect to the said reactants.

2. A process according to claim 1 in which the sodium acetylide is dissolved in liquid anhydrous ammonia.

3. A process for the preparation of 9-fluorenyl sodium which comprises effecting reaction between fluorene and sodium acetylide by bringing the reactants into contact with one another in a liquid medium which is inert with respect to the said reactants.

4. A process for the preparation of cyclopentadienyl sodium which comprises effecting reaction between cyclopentadiene and sodium acetylide by bringing the reactants into contact with one another in a liquid medium which is inert with respect to the said reactants.

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5. A process according to claim 4 in which the sodium acetylide is dissolved in liquid anhydrous ammonia.

6. A process according to claim 3 in which the sodium acetylide is dissolved in liquid anhydrous ammonia.

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