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ALKALI METAL DERIVATIVES OF ACETYLENIC HYDROCARBONS

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9 Claims. (Cl. 260—533)

This invention relates to the preparation of alkali metal derivatives of acetylene and other hydrocarbons of the acetylene series and the utilization of such alkali metal derivatives in the preparation of organic compounds.

The alkali metal derivatives of acetylene and other acetylenic hydrocarbons heretofore have been prepared by reacting the hydrocarbon with the alkali metal dissolved in liquid ammonia. Another method consists in directly reacting the hydrocarbon with the metal; for example, sodium acetylide may be made by contacting sodium with acetylene gas. The use of liquid ammonia has the objection that special apparatus and refrigeration is required, while acetylides made without the use of the liquid ammonia usually are slow to react with other reagents.

An object of the present invention is to provide an improved method for reacting acetylene and other acetylenic hydrocarbons with alkali metals to form the corresponding acetylides. A further object is to provide an improved method for preparing propiolic acids and homologs thereof. Still other objects will be apparent from the following description.

The above objects are attained in accordance with the herein described invention by first preparing a solution of an alkali metal addition compound of a polycyclic aromatic hydrocarbon, and reacting this addition compound solution with the acetylenic hydrocarbon. The resulting alkali metal compound of the acetylenic hydrocarbon then may be reacted with various reagents such as carbon dioxide, alkyl halides and the like, to prepare valuable products. In this method the alkali metal addition compound of the polycyclic aromatic hydrocarbon thus serves as carrier for the alkali metal. By this means, the formation of the desired alkali metal derivative not only is facilitated but the alkali metal acetylide thus formed generally is in a more reactive state than when prepared by direct reaction with the alkali metal. This increased activity facilitates and improves yields in further synthetic reactions.

Our novel method may be carried out by reacting the various acetylenic hydrocarbons with alkali metal addition compounds of polycyclic aromatic hydrocarbons as described above. For example n-heptine may be so reacted to form its alkali metal derivative, which, in turn may be reacted with reagents such as alkyl halides and carbon dioxide to form valuable products.

Alkali metal derivatives used as alkali metal carriers in accordance with the present invention may be obtained by the addition of an alkali metal to aromatic polycyclic hydrocarbons such as naphthalene, diphenyl, anthracene, acenaphthene, retene and the like, including their homologs. The preferred method of producing these reactive and soluble alkali metal derivatives was first described by N. D. Scott in U. S. Patent 2,027,000 and a continuation of this patent, U. S. Patent 2,019,832. Certain classes of ether solvents were found to have a very specific action in promoting the reaction of alkali metals with aromatic hydrocarbons to form these intermediate addition products which according to the present invention must be used in the dissolved state in the solvents in which they have been prepared. Ethers which have been found useful in preparing these alkali metal addition products include all polyethers and all mono ethers containing a $CH_3—O—$ group and in which the ratio of the number of oxygen atoms to the number of carbon atoms is not less than 1:4 and whose structures are stable in contact with the alkali metal and its aromatic hydrocarbon addition complex in question.

By "stable" ethers we do not mean that the ethers may not react in some reversible reaction with the alkali metal and/or aromatic hydrocarbon since indications are that the ethers in effecting the reactions may to some extent take part in the reaction, but the ether must not be broken up or form irreversible reaction products. Thus, for example, ethylene oxide may be considered a cyclic ether falling within the limitations given for the oxygen carbon ratio; however, it reacts, for instance, with sodium naphthalene and hence cannot satisfactorily perform the function required. There may be a very slow ether cleavage with some of the good solvents, but at a rate much slower than that of the desired reaction. In order to simplify the wording later, we further specify such ethers as are "effective" within my invention as being "stable" although as noted they may play some reactive role in causing the reactions to proceed.

Inert non-ether types of solvents, such as hydrocarbons or alkyl sulfides which do not react with the alkali metals and which in themselves are non-effective for the reactions, may be used as diluting agents for the effective ethers. There is, however, a minimum concentration for the effective ether in the non-effective solvents beyond which the reaction will not proceed. Thus, in general, the effective ether can be diluted with a non-reactive, non-effective hydrocarbon or ether up to four or five times its volume. If the dilution be as high as six to ten times the volume of the

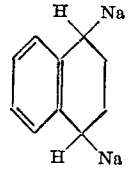
effective ether, the reaction to form the alkali metal addition product will not proceed.

By the use of these effective ethers alkali metals have been shown to add to aromatic hydrocarbons and certain hydroaromatic hydrocarbons containing more than one benzene nucleus as well as to certain nitrogen containing compounds such as n-methyl carbazol. Aromatic hydrocarbon compounds possessing a reactive methylene group are, of course, excluded from the list of hydrocarbons which will yield these addition compounds. For further description, the invention will be illustrated particularly with respect to the reaction of naphthalene with sodium, but it is to be understood that what is said thereon will apply equally well to the reaction of other alkali metals and to any of the suitable naphthalene homologues and analogues and other condensed ring systems which will allow these intermediates to form.

Effective ethers which fall within the specifications set forth above include dimethyl ether, methyl ethyl ether, ethylene glycol dimethyl ether, ethylene glycol methyl ethyl ether, ethylene glycol methyl butyl ether, ethylene glycol diethyl ether, ethylene glycol formal, glycerol formal methyl ether, the simple tri ethers of glycerol, tertiary amines and many others with similar properties which will function as solvents for the alkali metal intermediates and also mixtures of these ethers with non-effective solvents up to the concentration at which the effective ether ceases to exert its activating effect.

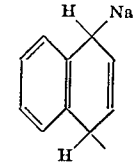
It is highly important that these effective ethers be essentially free from more than traces of hydroxyl or other impurities, which react with sodium to give especially those which yield insoluble compounds and which tend to "coat over" the surface of the metal, in order to get the addition reaction to start. The sodium should itself be clean and have been preserved under some inert solvent prior to use. The form of the sodium is immaterial, but cubes of the metal one fourth inch on an edge have been found quite satisfactory. Generally, even with the best of care in preparing the solvents, naphthalene and sodium, it is necessary to scratch the surfaces of these sodium cubes to initiate the formation of the green colored (in the case of naphthalene) sodium addition complex. A mechanical stirrer with sufficient speed to cause the sodium cubes to rub over each other lightly under the surface of a solution of naphthalene in one of the effective ethers will in a short time remove this thin protective film from the metallic surfaces and allow the reaction to proceed with great rapidity.

The effective ether solution of naphthalene will readily dissolve sodium in an amount equivalent to one gram atom of sodium for each gram molecule of naphthalene; thereafter the solution of further amounts of sodium becomes so slow as to be negligible. This is somewhat unexpected since the reaction products obtained by further treatment of the green sodium naphthalene complex, for example, with water or carbon dioxide, indicate that it is in large part the 1,4 disodium naphthalene:



It is probable that this is an equilibrium reaction. It is also found that other isomeric disodium addition compounds are formed as evidenced by the formation of isomeric acids upon treatment with carbon dioxide.

In view of the fact that the solution which is thus prepared, and contains one gram atom of sodium for each gram molecule of naphthalene, is a highly colored green solution and readily conducts the electric current, it is possible that the addition compound may exist in solution as a free radical which may be represented by the formula:



The soluble addition compound may involve the combination of disodium naphthalene with an extra molecule of naphthalene in some other manner. Its formula could be written,

$$Na_2C_{10}H_8—C_{10}H_8$$

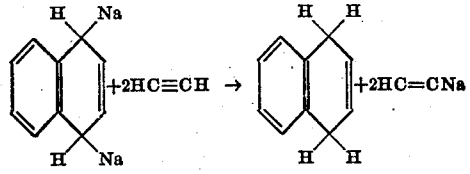
without specifying the exact method of combination. Moreover, this soluble addition product may conceivably also include some combination with the ether solvent to account for the specific action of the effective ethers. The reactions of these alkali metal addition products, however, are clearly evident and their use as intermediates is in no way limited by any hypothesis as to the probable structure in solution.

If such a solution which contains sodium equivalent to one gram atom of sodium for each gram molecule of naphthalene be treated with water or alcohol, it will yield equivalent amounts of naphthalene and dihydronaphthalene; with CO_2, it will yield the sodium salts of dihydronaphthalene dicarboxylic acids along with an equivalent amount of naphthalene. If, however, either the hydrolysis or the carboxylation is carried out gradually while further amounts of sodium are present in the liquid, further amounts of this sodium will dissolve as that in solution is used by the hydrolysis or carboxylation. In this manner, it is possible to react essentially all of the naphthalene and recover the major amount as dihydronaphthalene or dihydronaphthalene dicarboxylic acids.

The present invention is not restricted to the use of the above described ethers as solvents for the reaction between the polycyclic aromatic hydrocarbons and alkali metals. For example, certain amino compounds are also effective as solvents for promoting these alkali metal addition reactions. These amino compounds, which are described in co-pending applications filed by J. F. Walker and N. D. Scott, include the amines: trimethylamine, dimethyl ethylamine, and tetramethyl ethylene diamine and a variety of amino ethers having tertiary amino groups, such as dimethylamino dimethyl ether, dimethylaminoethyl methyl ether, diethylaminoethyl methyl ether, dimethylaminoethyl diether of ethylene glycol and diethylamino dioxan.

We will now proceed to describe the use of the above described sodium addition product of naphthalene as an intermediate or a form of dissolved sodium as a tool in the production of sodium acetylide and similar sodium derivatives of acetylenic hydrocarbons. We have discovered that when an acetylenic hydrocarbon is added to the green solution of sodium naph-

thalene in one of the above mentioned effective solvents, in general a metathesis reaction occurs in which the sodium atom is transferred to the position occupied by an acidic hydrogen of the hydrocarbon, with the formation of dihydronaphthalene as a by-product. The reaction between sodium naphthalene and acetylene is typical:



The resulting sodium acetylide is formed as a finely divided suspension in the solvent medium. This suspension is quite reactive and may be reacted with various reagents to produce valuable products. For example, it may be reacted with alkyl or aryl halides, with aldehydes or ketones, with halogens or with carbon dioxide. This method is especially well adapted for the production of propiolic acid by reacting the alkali metal acetylide suspension with carbon dioxide.

The following example will further illustrate the present invention:

Example

Acetylene was passed into a liter of dimethyl glycol ether at 15° C. containing the equivalent of 1.0 gram atom of sodium as sodium naphthalene. The green color was discharged after the requisite amount of acetylene had been absorbed with the simultaneous precipitation of monosodium acetylide as a white solid. The by-product 1,4 dihydronaphthalene remained dissolved in the ether. As soon as the sodium naphthalene had reacted completely, carbon dioxide was admitted and reacted to form sodium propionate. This salt was taken into water, acidified, extracted from water into ether and the ether removed in a vacuum. Forty-eight gms. of propiolic acid, 69% of theory, was recovered.

The alkali metal substitution compounds of acetylenic hydrocarbons prepared in accordance with our invention generally are produced in a very finely divided state and exist as a suspension of practically colloidal nature in the reaction medium in which they are formed. In this finely divided state, these alkali metal compounds exhibit a high degree of reactivity and in general are more reactive than are the same compounds made by other methods. For example, sodium acetylide made by reacting acetylene with sodium naphthalene addition compound existing as a finely divided suspension in the reaction solvent, is much more reactive than solid sodium acetylide made in the ordinary way and reacts very readily, for example, with carbon dioxide, to produce a high yield of propiolic acid. This high degree of reactivity makes these products especially advantageous as intermediates in organic syntheses.

The herein described method also is useful in preparing dihydro derivatives of the polycyclic aromatic hydrocarbons. In some cases this method results in improved yields of the dihydro compounds, with less polymer formation. For example, when dihydronaphthalene is prepared by reacting the sodium naphthalene addition compound with water more or less polymer of dihydronaphthalene is simultaneously formed. We have found that by reacting the sodium addition compound with acetylene, a substantially quantitative conversion to dihydronaphthalene is obtained, with substantially no polymer formation.

We claim:

1. The process comprising reacting an acetylenic hydrocarbon with a solution of an alkali metal addition compound of a polycyclic aromatic hydrocarbon in an activating solvent for the reaction.

2. The process comprising reacting an acetylenic hydrocarbon with a solution of a sodium addition compound of a polycyclic aromatic hydrocarbon in an activating solvent for the reaction.

3. The process comprising reacting acetylene with a solution of a sodium addition compound of a polycyclic aromatic hydrocarbon in an activating solvent for the reaction.

4. The process comprising reacting acetylene with a solution of a sodium addition compound of naphthalene in an activating solvent for the reaction.

5. The process comprising reacting n-heptine with a solution of a sodium addition compound of a polycyclic aromatic hydrocarbon in an activating solvent for the reaction.

6. The process comprising reacting an acetylenic hydrocarbon with a solution of an alkali metal addition compound of a polycyclic aromatic hydrocarbon in an activating solvent for the reaction, and thereafter reacting the resulting suspension of alkali metal compound with carbon dioxide.

7. The process comprising reacting acetylene with a solution of the sodium addition compound of a polycyclic aromatic hydrocarbon in an activating solvent for the reaction and thereafter reacting the resulting suspension of sodium acetylide with carbon dioxide.

8. The process comprising reacting acetylene with a solution of the sodium addition compound of naphthalene in an activating solvent for the reaction and thereafter reacting the resulting suspension of sodium acetylide with carbon dioxide.

9. The process comprising reacting n-heptine with a solution of the sodium addition compound of napthalene in an activating agent for the reaction and thereafter reacting the resulting suspension of sodium amyl acetylide with carbon dioxide.

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CERTIFICATE OF CORRECTION.

Patent No. 2,171,868. September 5, 1939.

NORMAN D. SCOTT, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 41, for "propionate" read propiolate; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 3rd day of October, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.