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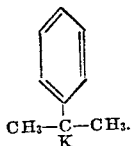
PREPARATION OF ALKALI METAL DERIVATIVES OF ORGANIC SUBSTANCES

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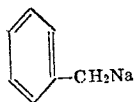
This invention relates to the use of highly reactive alkali metal addition compounds as intermediates in the preparation of alkali metal derivatives of acidic hydrogen containing organic compounds which either do not react directly with the alkali metal or else do so only with difficulty. This general type of metathesis reaction has already been the subject of much study. Ziegler et al., Ann. 473, 22 (1929), describes the use of potassium cumene,



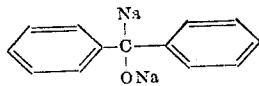
In Houben Weyl (1924) v. IV, p. 964, the preparation and use of lithium phenyl,



and sodium benzyl, are described. Other alkali

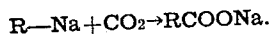


metal compounds employed include lithium, sodium or potassium methyl, ethyl, butyl, etc. All of these alkali metal compounds are substitution derivatives which are exceedingly difficult and costly to prepare. Certain ketones, which have no alpha hydrogen atom adjacent to the carbonyl group, also form alkali metal derivatives, e. g., sodium benzophenone,

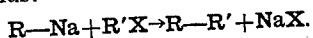


which can function as intermediates in the preparation of other alkali metal organic derivatives, Houben Weyl, (1924) v. IV, pp. 977-8.

Such alkali metal organic compounds are useful for a variety of organic syntheses. For example they may be reacted with carbon dioxide to produce organic acids, according to the reaction:



They also may be reacted with alkyl or aryl halides, thus:



An object of the present invention is to provide a convenient and economical method for producing alkali metal organic compounds. A further object is to provide improved methods for organic synthesis, including the production of carboxylic acids, in which organic alkali metal compounds are utilized as intermediates. Further objects will be apparent from the following description.

The above objects are attained in accordance with the hereindescribed invention by first preparing solutions of alkali metal addition compounds of polycyclic aromatic hydrocarbons, and reacting these addition compounds with other organic compounds having relatively acidic hydrogen atoms, whereby the desired alkali metal compounds of said other compounds are formed. These alkali metal compounds 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 compounds of the polycyclic aromatic hydrocarbons thus serve as carriers for the alkali metal. By this means, the formation of the desired alkali metal compounds not only is facilitated but the alkali metal compounds thus formed generally are 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.

The alkali metal derivatives used as alkali metal carriers in accordance with the present invention are obtained by the addition of alkali metals to aromatic polycyclic hydrocarbons such as naphthalene, diphenyl, anthracene, acenaphthene, retene and the like, including their homologs. The method of producing these reactive and soluble sodium derivatives was first described by 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 ether 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 noneffective 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.

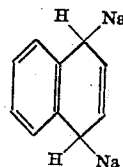
By the use of these effective ethers alkali metals have been shown to add to aromatic hydrocarbons and certain hydroaromatic hydrocarbons containing more than one benzene nucleus as well as to certain nitrogen containing compounds such as *n*-methyl carbazol. Aromatic hydrocarbon compounds possessing 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 noneffective 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

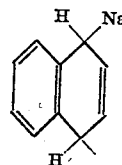
inert solvent prior to use. The form of the sodium is immaterial, but cubes of the metal one-fourth inch on an edge have been found quite satisfactory. Generally, even with the best of care in preparing the solvents, naphthalene and sodium, it is necessary to scratch the surfaces of these sodium cubes 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:

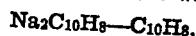


It is probable that this is an equilibrium reaction. It is also found that other isomeric disodium addition compounds are formed as evidenced by the formation of isomeric acids upon treatment with carbon dioxide.

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,



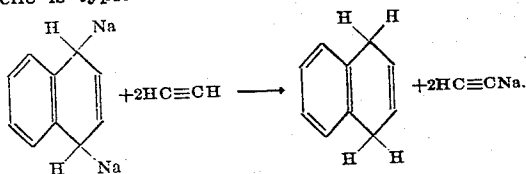
without specifying the exact method of combination. Moreover, this soluble addition product may conceivably also include some combination with the ether solvent to account for the specific action of the effective ethers. The reactions of these alkali metal addition products, however, are clearly evident 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 joint applications filed by N. D. Scott and J. F. Walker 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 this sodium addition product of naphthalene as an intermediate or a form of dissolved sodium as a tool in the production of other sodium-carbon compounds, sodium-oxygen-carbon compounds and sodium-nitrogen compounds otherwise difficult to prepare. We have discovered that when compounds possessing relatively acidic hydrogen atoms are added to the green solution of sodium naphthalene in one of the effective solvents, in general a metathesis reaction occurs in which the sodium atom is transferred to the position occupied by the acidic hydrogen with the formation of dihydronaphthalene as a by-product. The reaction between sodium naphthalene and acetylene is typical:



O. C. Dermer in Chemical Reviews, 14, 396 (1934) lists a series of weakly acidic compounds in a scale of descending acidities as follows:

- | | |
|-------------------------------------|--------------------------------|
| 1. Phenyl acetylene | 7. Triphenyl methane |
| 2. Indene | 8. 1-naphthyl diphenyl methane |
| 3. Phenyl fluorene | 9. Diphenyl methane |
| 4. Fluorene | 10. Cumene |
| 5. Xanthene | 11. Toluene |
| 6. Methyl diphenyl (phenyl toluene) | 12. Benzene |
| | 13. Ethane |

The sodium naphthalene addition compounds might be considered in this connection as substitution compounds of dihydronaphthalene. Their position in the preceding list would be above diphenyl methane but below triphenyl methane and they therefore will react in the manner indicated above with those compounds above diphenyl methane in the foregoing table.

The following examples further illustrate the present invention:

Example 1

Triphenyl methane, 0.1 gram molecule, was slowly added at room temperature to a green

solution of sodium naphthalene in the dimethyl ether of ethylene glycol made by adding 0.15 gram atom of sodium to 200 cc. of the ether containing 0.1 gram molecule of naphthalene. The color of the ether solution changed from green to brilliant red as the triphenyl methane was added. Carbon dioxide was then admitted until this red color was discharged. Water was added to dissolve out the sodium salt of triphenyl acetic acid. By acidification with dil. HCl, 23.3 grams or an 81.0% yield, of triphenyl acetic acid having an equivalent weight of 286 was obtained.

Example 2

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 propionic acid, 69% of theory, was recovered.

Example 3

Tertiary butanol, 1.0 gram molecule, was slowly added to a stirred solution of naphthalene, 1.0 gram molecule in 500 cc. of dimethyl glycol ether in which the naphthalene was slowly reacting with one gram atom of sodium to form the soluble green sodium naphthalene addition product. The rate of addition of the tertiary butanol was such that the green color of the reaction mixture was discharged practically as fast as it was formed, allowing only a faintly green color to build up in the dimethyl glycol ether solution. The reaction was essentially quantitative, i. e., one gram molecule of tertiary butanol was required to completely discharge the green color, thereby indicating that the whole gram atom of sodium had been consumed. The slurry of sodium tertiary butylate obtained by distilling off the glycol dimethyl ether and adding petroleum ether, b. p. 40-60° C., was filtered, washed with more petroleum ether, and carefully dried. The equivalent weight of the dried sodium tertiary butylate by titration was 87.3.

Example 4

Fluorene, 0.1 gram molecule, dissolved in 100 cc. of dimethyl glycol ether was added slowly to a solution of 0.1 gram molecule of naphthalene in 200 cc. more of the dimethyl glycol ether in which the sodium naphthalene addition product was slowly forming by the interaction of the naphthalene with an excess of sodium at 20° C. As the addition of the fluorene solution continued, the reaction mixture changed from green to a yellowish brown colored solution from which a precipitate of yellow sodium fluorene separated. After the sodium reaction was completed, carbon dioxide was passed through the reaction mixture. The sodium carboxylate formed was dissolved in water and the aqueous solution treated with HCl to precipitate the free carboxylic acid. A yield of 9.8 grams of recrystallized fluorene-9-carboxylic acid was obtained, m. p. 224° C. and having a neutralization equivalent of 212.

Example 5

Acetonitrile, 20.5 grams, was added to a solution of sodium naphthalene (equivalent to 14 grams sodium) in 250 cc. of dimethyl ether at -50° C. As soon as the acetonitrile had been added, n-butyl bromide, 69 gms., was introduced slowly keeping the temperature between -25 and -30° C. The yield of capronitrile, b. p. 160-165° C., was 38 grams.

Example 6

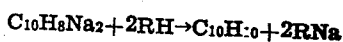
A quantity of standard solution of aniline in dimethyl glycol ether (0.240 molal) was titrated into a dilute solution of sodium naphthalene in the same solvent. 28 cc. of this aniline solution were required to completely discharge the green color which changed to a violet red toward the end of the titration and then finally to colorless. The sodium content of the amount of sodium naphthalene solution used was then determined by titrating the alkalinity as being equivalent to 32 cc. of 0.227 normal acid. The reaction ratio of aniline and sodium naphthalene is thus shown to be 1:0.93.

Example 7

One gram equivalent of phenyl acetic acid was added to a solution of sodium naphthalene in dimethyl glycol ether containing two gram equivalents of sodium. The sodium reaction product was soluble and imparted a brilliant purple color to the solution. This solution then absorbed carbon dioxide to give the disodium salt of phenyl malonic acid. The isolated free acid had an equivalent weight of 83 and a melting point of 153-4° C. with gas evolution.

Other compounds which will react quantitatively with sodium naphthalene and other alkali metal addition compounds of polycyclic aromatic hydrocarbons include for example, capronitrile, pyrrole, pyrrolidine, piperidine, dibenzalacetone, etc. It is evident from the foregoing examples that the method is applicable to the preparation of the sodium derivative of any organic compound which will react with the sodium addition compound of an aromatic polycyclic hydrocarbon to replace a hydrogen atom of the organic compound with a sodium atom and obviously is not limited to the cases just cited.

In general, it may be stated that an alkali metal addition compound of a polycyclic aromatic hydrocarbon will react with those organic compounds which contain one or more hydrogen atoms which are more acidic in nature than the hydrogen atoms of the polycyclic aromatic hydrocarbon utilized and this reaction results in a substitution of the acidic hydrogen atom or atoms by alkali metal, the replaced hydrogen atom taking the place of the alkali metal in the addition compound. Thus, using the sodium addition compound of sodium naphthalene, the reaction may be represented:



The various organic compounds which thus may react with the alkali metal addition compounds of polycyclic aromatic hydrocarbons and their homologs include cyclic hydrocarbons such as fluorene and indene, acetylene and other acetylenic hydrocarbons, carboxy acids, alcohols, phenols, primary and secondary amines, (both aryl and alkyl amines), dialkyl and aryl alkyl ketones, nitriles and acid amides. The products of these reactions, which are alkali metal sub-

stitution compounds, are useful intermediates for various organic syntheses. For example, they may be reacted with carbon dioxide to form carboxy acids, with alkyl halides and other organic halogen compounds and with various other compounds. These alkali metal substitution compounds 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 acetylides 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 acetylides 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 reactions also are 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 for preparing an alkali metal organic compound by replacing at least one hydrogen atom of an organic compound with an alkali metal atom which comprises reacting an organic compound having a replaceable hydrogen atom with an alkali metal addition compound of a polycyclic aromatic hydrocarbon, said alkali metal addition compound being dissolved in an activating solvent for the reaction.
2. The process for preparing an alkali metal organic compound by replacing at least one hydrogen atom of an organic compound with an alkali metal atom which comprises reacting an organic compound having a replaceable hydrogen atom with a sodium addition compound of a polycyclic aromatic hydrocarbon, said sodium addition compound being dissolved in an activating solvent for the reaction.
3. The process for preparing an alkali metal organic compound by replacing at least one hydrogen atom of an organic compound with an alkali metal atom which comprises reacting an organic compound having a replaceable hydrogen atom with a sodium addition compound of naphthalene, said sodium addition compound being dissolved in an activating solvent for the reaction.
4. The process for replacing a hydrogen atom of a hydrocarbon with an alkali metal atom to produce an alkali metal substitution compound of said hydrocarbon which comprises reacting said hydrocarbon with an alkali metal addition compound of a polycyclic aromatic hydrocarbon, said alkali metal addition compound being dissolved in an activating solvent for the reaction.
5. The process comprising reacting fluorene

with a solution of the sodium addition compound of a polycyclic aromatic hydrocarbon said sodium addition compound being dissolved in an activating solvent for the reaction.

6. The process comprising reacting a solution of the alkali metal addition compound of a polycyclic aromatic hydrocarbon with an organic hydroxy compound said alkali metal addition compound being dissolved in an activating solvent for the reaction.

7. The process comprising reacting an alcohol with a solution of the alkali metal addition compound of a polycyclic aromatic hydrocarbon said alkali metal addition compound being dissolved in an activating solvent for the reaction.

8. The process comprising reacting a solution of the alkali metal addition compound of a polycyclic aromatic hydrocarbon with an amino compound selected from the group consisting of primary and secondary amines said alkali metal addition compound being dissolved in an activating solvent for the reaction.

9. The process comprising reacting a solution of the sodium addition compound of naphthalene with an amino compound selected from the group consisting of primary and secondary amines said sodium addition compound being dissolved in an activating solvent for the reaction.

10. The process comprising reacting aniline with a solution of the sodium addition compound

of naphthalene said sodium addition compound being dissolved in an activating solvent for the reaction.

11. The process for replacing a hydrogen atom of a hydrocarbon with an alkali metal atom to produce an alkali metal substitution compound of said hydrocarbon which comprises reacting said hydrocarbon with a sodium addition compound of a polycyclic aromatic hydrocarbon, said sodium addition compound being dissolved in an activating solvent for the reaction.

12. The process for replacing a hydrogen atom of a hydrocarbon with an alkali metal atom to produce an alkali metal substitution compound of said hydrocarbon which comprises reacting said hydrocarbon with a sodium addition compound of naphthalene, said sodium addition compound being dissolved in an activating solvent for the reaction.

13. The process comprising reaction fluorene with a solution of the sodium addition compound of a polycyclic aromatic hydrocarbon and reacting the resulting suspension of the sodium compound of fluorene with carbon dioxide said sodium addition compound being dissolved in an activating solvent for the reaction.

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