[CONTRIBUTION FROM THE LABORATORIES OF THE R. & H. CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

Sodium Naphthalene. I. A New Method for the Preparation of Addition Compounds of Alkali Metals and Polycyclic Aromatic Hydrocarbons

BY N. D. SCOTT, J. F. WALKER AND V. L. HANSLEY

The direct reaction of alkali metals with certain aromatic hydrocarbons has been reported previously in the literature, the reaction of sodium with anthracene in ethyl ether solution[1] being an example. Efforts to extend this reaction to simpler hydrocarbons such as naphthalene and diphenyl have met with very limited success. Schlenk and Bergmann were able to cause lithium to react with these hydrocarbons to a sufficient extent to make some examination of the products[2] but reported no detectable reaction with sodium under similar conditions.

A solution of sodium in liquid ammonia also has been used to bring about the addition of sodium to naphthalene but in this case the reaction is complicated by the rapid ammonolysis of the products.[3] Liquid ammonia as a solvent has the added disadvantage of reacting with carbon dioxide, interfering with the use of this reagent in characterizing the sodium compounds.

We have found that when methyl ether is used as the solvent medium the previously known sodium reactions take place many times faster than in ethyl ether. Furthermore, with this solvent it is possible to increase the scope of the reaction to include naphthalene and diphenyl as well as many other aromatic hydrocarbons. This striking difference of methyl ether compared with ethyl ether is more than a difference in the rate of the reaction, for if ethyl ether is added to a solution of sodium naphthalene in dimethyl ether the rate of formation of the sodium compound is gradually decreased. If sufficient ethyl ether is added the formation of the sodium compound is inhibited completely and the compound already formed decomposes with the liberation of the original hydrocarbon and elementary sodium. With concentrated solutions of hydrocarbons in pure methyl ether it is possible to dissolve one or two gram atoms of sodium per liter in two hours or less. It is already known that the first member of most homologous series of organic compounds shows the more characteristic properties of the series to a unique degree but the surprising difference between methyl ether and ethyl ether has not been fully appreciated by previous investigators. Methyl ethyl ether is the only other monoether in which these reactions occur readily. The formation of sodium naphthalene is slow but detectable in the methyl propyl ethers.[4]

In seeking for suitable solvents that are liquid at ordinary temperatures, we discovered that the dimethyl ether of ethylene glycol (b. p. 85°) is substantially equivalent to dimethyl ether as a solvent for sodium reactions. Contrary to the conclusions that might have been drawn from the behavior of monoethers it was found that all fully alkylated glycols and polyhydric alcohols are effective solvents for sodium addition reactions.[5] It was also found that trimethylamine and a few other amino compounds are effective although they offer little advantage over the ethers.

For most purposes dimethyl ether and the dimethyl ether of ethylene glycol are the most suitable solvents for the reaction, and the latter is the more convenient by reason of its boiling point. It is, however, slowly attacked by sodium naphthalene at room temperature with the formation of methyl vinyl ether, presumably in accordance with the equation

$$C_{10}H_8Na_2 + 2CH_3OCH_2CH_2OCH_3 \longrightarrow C_{10}H_{10} + 2CH_3ONa + 2CH_3OCH{=}CH_2$$

The methyl vinyl ether was identified by its boiling point and unsaturation toward bromine.

The presence of the special solvent is required not merely for the initiation of the reactions but for the existence of sodium naphthalene. This can be shown by preparing a solution of sodium naphthalene in dimethyl ether and then completely evaporating the ether at room temperature. The dark green solution deposits a very dark green solid which changes to gray in color with loss of the last traces of ether. The solid will then on treatment with water evolve nearly the theoretical amount of hydrogen as such. When sodium naphthalene solution is treated with water no hy-

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(1) Schlenk, Appenrodt, Michael and Thal, *Ber.*, **47**, 479 (1914).

(2) Schlenk and Bergmann, *Ann.*, **463**, 91 (1928).

(3) Wooster and Smith, THIS JOURNAL, **53**, 179–187 (1931).

(4) Scott, U. S. patent 2,019,832 (1935).

(5) Scott, U. S. patent 2,023,793 (1935).

drogen is evolved. If the solid be extracted with heptane a residue is obtained consisting almost entirely of sodium. For most purposes the isolation of sodium naphthalene in the solid state is not attempted since its reactions are conveniently carried out in solution.

The special solvents which are effective for the reaction of sodium with naphthalene can be used in similar fashion with the other alkali metals. In place of naphthalene one may use methyl naphthalenes, acenaphthene, diphenyl or phenanthrene, none of which react with sodium in ethyl ether solution. The special solvents also have a striking effect in facilitating the addition reactions of sodium with anthracene and with benzophenone, causing much more rapid reaction than occurs in ethyl ether. The special solvents do not appear to facilitate the reaction of sodium with hydrocarbons such as triphenylmethane, fluorene, or acetylene where the characteristic reaction is one of substitution.

Solutions of sodium naphthalene display many unusual properties. The solutions are dark green in color and have good electrical conductivity. No quantitative measurements have been made of the heat of the reaction by which they are formed, but it is not large. This is consistent with the ease of dissociation of the compound either by removing the ether solvents by evaporation or by dilution with a large volume of hydrocarbon solvent, or by removing the sodium, for example by shaking with mercury. The amount of sodium which will dissolve readily in a solution of naphthalene or diphenyl is only one atom per molecule of hydrocarbon. Inasmuch as many of the reactions of the solution correspond with a disodium naphthalene addition compound, this raises the question of the formula of the compound. The formula $C_{10}H_8Na_2 \cdot C_{10}H_8$ correctly represents the proportions of sodium and naphthalene while avoiding the question of structure. Discussion as to structure will largely be deferred to later papers dealing more fully with the reactions.

The reactions of sodium naphthalene can be divided into two classes. In the first the naphthalene is recovered unchanged, the solution behaving much like dissolved sodium. In this class one may mention the reactions with mercury, with oxygen, and with benzyl chloride. In the second class of reactions the naphthalene is reduced to dihydronaphthalene or its derivatives depending on the reagent used. With water, alcohols or the wide range of organic compounds capable of forming sodium derivatives where sodium replaces hydrogen, the products are dihydronaphthalene and the sodium compound of the material used as source of hydrogen. For example with acetylene the reaction can be represented by the equation

$$C_{10}H_8Na_2 \cdot C_{10}H_8 + 2C_2H_2 \longrightarrow C_{10}H_{10} + C_{10}H_8 + 2C_2HNa$$

This is a convenient method for the preparation of a variety of sodium derivatives.

In general, the only requirements for the formation of sodium naphthalene and related compounds in dimethyl ether and other active ether solvents are that the solvent be pure and dry and that the hydrocarbon be reasonably pure. It is also imperative that a clean surface of alkali metal be exposed to initiate the reaction. Once started, the reaction thoroughly cleans any metal surface that was not originally clean. When pieces of sodium that are reacting come in contact in the reaction mixture, they fuse together, even at −30° and lower. Impurities such as water, methanol and carbon dioxide prevent the reaction from starting by forming products which coat the surface of the alkali metal as soon as it is exposed. If they are only present in traces, however, persistent scratching of the metal surface will eventually lead to their destruction and the reaction will proceed.

Experiments

Preparation of Sodium Naphthalene Solutions

A. In Dimethylglycol Ether.—One liter of a molal solution of naphthalene in pure dry dimethyl glycol ether is placed in a two-liter three-necked flask equipped with a mercury-sealed stirrer in which an atmosphere of pure dry nitrogen is maintained. About 25 g. of sodium is then added, the metal being cut in the form of sticks 2–3 cm. long and 3–5 mm. square on the end. After the sodium has been added the mixture is agitated mechanically. The stirring should be rapid at the start but should be decreased considerably after the reaction has commenced. With a good grade of dimethylglycol ether the reaction should start in one to three minutes. Some cooling is required, and this can be accomplished safely by the use of a methanol cooling bath to which solid carbon dioxide is added as required. The reaction mixture should be kept between −10 and +30°. At temperatures below −10° the reaction rate falls off considerably in dimethylglycol ether. At 20–25° the reaction is complete in about two hours. Unreacted sodium which is usually stuck together in a single piece can then be removed easily from the mixture with forceps.

The progress of the reaction can be measured from time to time by removal of small samples of the reaction mixture and determination of their sodium content, after dilution with alcohol, by titration with standard acid using methyl red. This does not discriminate between sodium naphthalene and other suspended or dissolved alkaline sodium compounds in the solution but when pure solvent is used it gives a close approximation of the sodium naphthalene that has been formed.

B. In Dimethyl Ether.—The preparation of sodium naphthalene in dimethyl ether is carried out in much the same way as in dimethylglycol ether except for the changes occasioned by the low boiling point (−25°). The flask in which the reaction is to be carried out is cooled to about −50° in a bath of solid carbon dioxide and methanol, and the solvent is led in as a gas from a cylinder and condensed. The reaction is best carried out at a temperature of −30°. The nature of the solvent makes it difficult to make analyses in this case, but an approximate measure of the reacted sodium can be obtained easily by weighing the unreacted sodium recovered after the completion of the reaction.

Dimethylglycol Ether.—This reagent was prepared by the methylation of the monomethyl ether of ethylene glycol. It must be purified and thoroughly dried for use in alkali metal reactions. It is a colorless fluid with a characteristic ether-like odor boiling at 85°.

Dimethyl Ether.—This ether was sufficiently pure as obtained from the Ammonia Department of E. I. du Pont de Nemours & Company, Inc.

Summary

The reaction of aromatic hydrocarbons with sodium is so greatly facilitated by employing dimethyl ether or dimethylglycol ether as the solvent, in place of diethyl ether, that with the use of these special solvents even such hydrocarbons as naphthalene and diphenyl can be converted easily into sodium compounds.

NIAGARA FALLS, N. Y. RECEIVED SEPTEMBER 23, 1936

[CONTRIBUTION FROM THE BURROUGHS WELLCOME AND CO., U. S. A., EXPERIMENTAL RESEARCH LABORATORIES]

The Separation of Primary Aryl Amines from Secondary Alkylaryl Amines

BY CLAYTON W. FERRY AND JOHANNES S. BUCK

In the course of the preparation of a series of unsymmetrical alkylaryl ureas and thioureas[1,2] a number of secondary alkylaryl amines, substantially free from primary aryl amines, was required (small amounts of tertiary amines are unimportant, since they form no ureas). When alkoxy and certain N-alkyl groups are present in the secondary amine, the usual methods of preparation (*e. g.*, *via* the acyl derivatives, nitroso compounds, etc.) are not satisfactory[2] and it is necessary to alkylate the primary aryl amine directly and to remove unchanged primary amine from the product. A method for carrying out this removal, suggested by the work of Eibner and by several patents[3] and outlined by DeBeer, Buck, Ide and Hjort[2] is here described, whereby the primary amine is removed readily by shaking the crude secondary amine with benzaldehyde–sodium bisulfite compound and water. The primary amine combines with the reagent and is recoverable, while the secondary amine remains unattacked.

Experimental

Twenty grams each of primary aryl amine and secondary alkylaryl amine (the secondary amines mentioned in this report were all purified *via* the nitroso compound) were mixed and shaken mechanically with water and benzaldehyde-sodium bisulfite compound at room temperature. The mixture was then filtered from the solid with suction, the solid well washed with ether and the filtrate extracted with ether. The total ether was washed with brine, the ether evaporated and the residual amine tested for primary amine.

In the first series of experiments, designed to investigate the conditions of reaction, the above process was repeated until tests showed the absence of any appreciable amount of primary amine (< 0.5%). In the first treatment 50 cc. of water and one mol of bisulfite compound (calculated on the primary amine present) were used. In the second treatment 30 cc. of water and 0.5 mol of bisulfite compound and in the third and subsequent treatments, 30 cc. of water and 0.25 mol of bisulfite compound were used. In all cases the shaking was for two hours per treatment.

When this method was applied to mixtures of methyl aniline, *n*-butylaniline, ethyl-*m*-toluidine, ethyl-*p*-toluidine and ethyl-*o*-phenetidine, with the corresponding primary amine, over 80% of the secondary amine, containing less than 0.5% of the primary amine was obtained after the third treatment. Similar mixtures from ethyl-*p*-phenetidine and isopropyl-*p*-anisidine required, respectively, four and five treatments, about 54% of the secondary amine being recovered. A mixture from ethyl-*o*-toluidine was not purified to less than 10% of primary amine, even after five treatments.

The second series of experiments was carried out in order to simplify the process practically, and to reduce the losses in manipulation. It was found that, using the same mixture (20 g. primary amine, 20 g. secondary amine), efficient separation could be obtained by six hours of shaking

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[1] Buck, Hjort and DeBeer, *J. Pharmacol.*, **54**, 188 (1935).

[2] DeBeer, Buck, Ide and Hjort, *ibid.*, **57**, 19 (1936).

[3] German Patent 181,723, 132,621, 157,909; Eibner, *Ann.*, **316**, 89 (1901).