Summary

p-Nitrobenzyl chloride is a useful reagent for the identification of alkyl barbituric acids. It reacts with these acids, in the presence of sodium carbonate, to form crystalline substitution products with definite melting points. It reacts not only with the imide hydrogens but also with the methylene hydrogens to give completely substituted derivatives.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF CORNELL COLLEGE AND THE UNIVERSITY OF IOWA]

FACTORS INVOLVED IN THE PREPARATION OF MERCURY DI-ISOBUTYL BY THE REACTION OF FRANKLAND AND DUPPA

BY HARRY F. LEWIS AND EUNICE CHAMBERLIN

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In connection with an investigation involving the preparation of the sodium alkyls, it became necessary to make a large quantity of mercury di-*iso*butyl.[1] The mercury dialkyls have been known since the time of Frankland and Duppa,[2] who prepared mercury dimethyl and mercury diethyl by the action of dilute sodium amalgam on the alkyl iodide in the presence of ethyl acetate. The preparation of mercury di-*iso*butyl by this reaction has been studied in some detail and the results are given in this paper.

Other dialkyls prepared by the same reaction include the di-*iso*butyl,[3] the di-octyl,[4] the di-*n*-butyl,[5] and the dipropyl and di-*iso*propyl derivatives.[6] More recently, Marvel and Gould[7] have prepared the methyl, ethyl, *n*-propyl, *iso*propyl and *n*-butyl mercury di-alkyls through the use of the Grignard reagent with the mercuric halide, and Marvel and Calvery[8] the di-*sec.*-butyl, di-*sec.*-octyl, di-*tert.*-butyl and di-*tert.*-amyl derivatives.

Discussion of Experimental Work

In developing the best conditions for the preparation of mercury di-*iso*butyl by the Frankland and Duppa reaction, a number of variables

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[1] It is needless to add that mercury di-*iso*butyl is extremely poisonous. The compound is volatile and ill effects are not noticed at the time. Symptoms of poisoning include severe headaches, disorder of the digestive tract and a sensitivity both toward the odor and taste of the compound in the atmosphere of the laboratory. Continued exposure to the action of the mercury alkyls may result in a degeneration of the central nervous system and brain.

[2] Frankland and Duppa, *J. Chem. Soc.*, **16**, 415 (1863); *Ann.*, **130**, 104 (1864).

[3] Cahours, *Compt. rend.*, **76**, 133 (1873).

[4] Eichler, *Ber.*, **12**, 1880 (1879).

[5] Tiffeneau, *Bull. soc. pharmacol.*, **28**, 65 (1921).

[6] Goret, *ibid.*, **29**, 197 (1922).

[7] Marvel and Gould, THIS JOURNAL, **44**, 153 (1922).

[8] Marvel and Calvery, *ibid.*, **45**, 820 (1923).

were studied. These include the influence of time of reaction and temperature, relative concentrations of alkyl halide, amalgam and ethyl acetate, the replacement of iodide by bromide and of ethyl acetate by other esters and other compounds containing the carbonyl group.

Standard Procedure

The standard procedure developed as best for the preparation of mercury di-*iso*butyl is as follows.

A 2-liter round-bottomed flask is set up in an ice-bath and equipped with a 150-cc. dropping funnel, thermometer, reflux condenser and mechanical stirrer. The noncondensable gases are passed through cold concentrated sulfuric acid and then through a spiral condenser at −10°. In the flask are placed 0.294 mole (31 cc.) of *iso*butyl iodide and 0.147 mole (14.3 cc.) of ethyl acetate. When the mixture cools to the temperature of the ice-bath, a 0.25% sodium amalgam made by adding 0.591 mole (13.6 g.) of sodium to 27.2 moles (5440 g. or 400 cc.) of mercury is run in at such a rate that the temperature of the mixture does not go above 15°. The amalgam in the dropping funnel is protected from moisture in the air by means of a calcium chloride tube.

When the amalgam is added (this takes about forty-five minutes), the flask is disconnected, a layer of ether added and the excess sodium in the amalgam destroyed by the addition of water. The layers are separated in a thick-walled separatory funnel, the ether layer is dried with calcium chloride and fractionally distilled. Mercury di-*iso*butyl is collected between 202 and 206°.

Variables

Time.—The desired reaction appears to proceed rapidly and is complete as soon as the last of the amalgam has been added. Under the standard conditions a yield of 56.5% of mercury di-*iso*butyl is obtained. Refluxing the mixture until the total reaction time is two hours does not increase this yield.

Temperature.—Low temperatures favor the formation of the mercury di-*iso*butyl to a slight extent. With temperatures between 0–5° the yield is 56.5%, between 15–20°, 49% and at the reflux temperature (75–85°) it falls off to 45%.

Molecular Ratio of Reagents

Sodium.—A variation in quantity of sodium, the other factors being kept constant, is permissible to a certain degree. In the standard procedure, two moles of sodium to one of *iso*butyl iodide are used. Doubling the quantity of sodium to increase the ratio to 4:1 brings the yield down from 56.5 to 50.7%. When the ratio is decreased from 2:1 to 1.1:1, the yield is 48.7%. This is about the lowest ratio to give good results and indicates that a molar concentration of 1:1 moles of sodium may be used when the concentration of the amalgam is approximately 0.14% by weight.

Molar Ratio of Mercury.—Considerable decrease in yield is noted when the volume of mercury is doubled while the weight of sodium is constant. When 800 cc. of mercury is amalgamated with the standard amount of sodium, the weight concentration of the amalgam becomes 0.125%; this amalgam gives but 38.3% of mercury di-*iso*butyl.

Nature and Amount of Catalyst.—A half mole of ethyl acetate referred to the iodide (ratio 1:2) gives the optimum yield of 56.5%. A molar ratio of 1:1 gives but 48.7%; on the other hand, a ratio of 1:10 (*cf.* Tiffeneau, ref. 5) forms but small quantities of the desired product.

In the absence of ethyl acetate, mercury di-*iso*butyl is not formed.

A 1:1 ratio of ethyl butyrate with *iso*butyl iodide gives a 45% yield, while the 1:2 ratio forms but 20.4%.

Catalysts Other than Esters.—Other substances containing the carbonyl radical may be used as catalysts in place of the esters. Such substances include aldehydes, ketones and anhydrides.

Acetone.—A 1:1 molar ratio of acetone to *iso*butyl iodide gives a 50% yield of mercury di-*iso*butyl, while a 1:2 ratio forms 42.7%.

Isovaleraldehyde.—*Iso*valeraldehyde will also act as a catalyst in the production of the desired compound but the formation of condensation products interferes with the separation of the mercury di-*iso*butyl.

Smaller amounts of mercury di-*iso*butyl result when the ester is replaced by acetic anhydride.

It would thus appear that the carbonyl radical plays an important part in the formation of mercury di-*iso*butyl from the action of sodium amalgam on *iso*butyl iodide. This enlarges the statement found in the literature to the effect that "the reaction takes place only in the presence of an ester like methyl or ethyl acetate."[9]

The function of the carbonyl compound is uncertain. In many cases it is apparently used in the reaction and may not be entirely recovered.

Use of Isobutyl Bromide.—When the iodide is replaced by the bromide and the reaction carried out as usual, either for forty-five minutes or for a much longer period, only traces of mercury di-*iso*butyl are obtained; the bromide in these cases may be recovered unchanged.

It makes very little difference whether the amalgam is added to the mixture of catalyst and iodide or whether the reverse procedure is used. The yield is the same in either case. The standard procedure is preferred since it is easier to stir the mixture when it is added in this order.

In the original method as proposed by Frankland and Duppa, the reagents were all shaken together in a separatory funnel. This is difficult to accomplish when large quantities of amalgam are used. It is also hard to control experimental conditions and so the yields are found to vary.

The principal by-product in the reaction is di-*iso*butyl formed as the result of the Wurtz reaction. There is no evidence of the formation of *iso*butane and very little for the presence of *iso*butene among the reaction

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[9] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, p. 26–27.

products. A purple color in the sulfuric acid wash bottle suggests that the iodide is being carried over.

Conclusions

1. A convenient method has been described for preparing mercury di-*iso*butyl by the method of Frankland and Duppa. Yields of 50–55% may be obtained.
2. Other esters may be used in place of ethyl acetate. The discovery has been made that carbonyl compounds other than esters can be used as catalysts in the reaction.
3. The principal by-product is di-*iso*butyl formed by the Wurtz reaction between sodium and *iso*butyl iodide.
4. Bromide may not replace iodide under the experimental conditions described.
5. Optimum yields are obtained when the following molar concentrations are used: one mole of *iso*butyl iodide, two moles of sodium, one half mole of ethyl acetate or one mole of acetone and forty six moles of mercury.

MOUNT VERNON, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 591]

THE DISRUPTION OF THE CORN STARCH GRANULE AND ITS RELATION TO THE CONSTITUENT AMYLOSES[1]

BY T. C. TAYLOR AND C. O. BECKMANN

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In some earlier work in this Laboratory, a method for separating the amyloses in corn starch was devised[1a] and the amount of the insoluble or α-amylose and the soluble or β-amylose determined for corn and other starches. This separation, like all other separations, has as its first step the disruption of the granule in water in order to make available the constituent amyloses in the resulting paste. The completeness of the disruption in this case was gaged by the absence of the characteristic granules under the microscope. To obtain the proper type of paste it was necessary to pre-treat the starch with alcoholic hydrogen chloride and then use an effective swelling agent like ammonium thiocyanate to break open the granules when water was added subsequently.

The primary purpose of this paper is to show that the amount of the amyloses in a given starch, such as that of corn, is not dependent on any specific chemical action of the above reagents but only on their effective-

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[1] The work covered in this paper is taken from a part of a dissertation presented by C. O. Beckmann to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[1a] Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).