

as amylsodium.<sup>1</sup> The major differences between these chlorides and the lower members of the series are the greater tendency of the reaction mixtures to gel and the occurrence of a pink to gray-white color in place of a blue during the condensation. No evidence could be found of any true solution of these substances in petroleum ether.

### Summary

*n*-Octylsodium and *n*-decylsodium have been prepared by condensation in petroleum ether. The yields and properties were similar to those observed with amylsodium rather than with propyl- or butylsodium.

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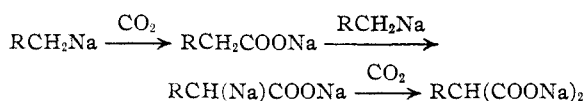
## Condensations by Sodium. XXII. The General Theory of the Wurtz Reaction. The Initial Step

BY AVERY A. MORTON, JOHN B. DAVIDSON AND HERBERT A. NEWBY

This and the following communication record results of a critical inquiry into the mechanism of the Wurtz reaction, particularly as regards the issue of a free radical *vs.* an organometallic intermediate. The latter is deemed adequate. This first paper will show that there is no need for assuming existence of a free radical prior to formation of this organo-sodium compound; the second will show there is no need afterward. The contention that the organometallic intermediate can be regarded as the sole necessary first product will be based on the facts that (a) there is only one organosodium compound formed, and (b) it is formed in essentially quantitative yield. A view that the sodium metal serves as a trap for the free radical is judged unnecessary.

**The Organosodium Compound.**—The excellent work of Gilman and Pacevitz,<sup>1</sup> in which the organosodium compound was poured on solid carbon dioxide, has shown that there was one amyl radical for every combined sodium atom rather than a mixture of amylsodium and an "amylidene disodium" as previously assumed.<sup>2</sup> Their results have been confirmed in this Laboratory, not only with amylsodium, but also with butylsodium which has shown<sup>3</sup> a greater tendency to form a malonic acid under ordinary conditions of carbonation, *i. e.*, when passing carbon dioxide into the mixture. The result is important because it brings the mechanism of formation of alkylmalonic acids into line with that previously observed<sup>4</sup> for phenylmalonic acid, in that the di-

carboxylic acid is a product of a secondary reaction according to the equation



It is of particular value to this discussion because it eliminates any necessity for assuming the intermediate free radical which accounted for the supposed disodium compound.

**The Quantitative Yield.**—The higher the yield of organosodium compound, the more obvious the two phases of the reaction. A good yield depends on (a) presence of excess sodium in a finely divided state, (b) absence of a protective coating on the metal and (c) an unreactive carbon-halogen bond.

The first requirement is met by adding the halide to the sodium which is as finely divided as possible and is being agitated vigorously. In earlier work<sup>1</sup> with amyl chloride and sodium, the conversion to an organosodium compound was 95% when one-fifth equivalent of chloride was added and was 63% when an equivalent had been used. We have now raised the final yield to 72% by improved agitation using a stirrer at 10,000 r. p. m. The trend is unmistakably toward 100% yield.

The second requirement of no protective coating is best realized with a primary alkyl chloride. As seen under a microscope, a primary alkyl chloride produces an insoluble, colloidal, jelly-like mass that usually appears to be pushed out rapidly as a broad band from the interior of a small but seemingly inexhaustible particle of sodium. Characteristic shapes are drawn in Fig. 1. Occasional

(1) Gilman and Pacevitz, *THIS JOURNAL*, **62**, 1301 (1940).

(2) Morton and Richardson, *ibid.*, **62**, 123 (1940).

(3) Morton, Hallowell and Richardson, *ibid.*, **63**, 327 (1941).

(4) Morton and Fallwell, *ibid.*, **60**, 1426 (1938).

eruptions give evidence of a vigorous reaction and of the ability of the chloride to penetrate the colloidal mass rapidly and sustain the rate. In contrast to this ease of contact between halide and metal, the secondary chloride forms an apparently hard and impenetrable coating. No reaction is visible. This difference in the surface coatings probably explains the observations of Richards<sup>5</sup> who found the reaction of ethyl iodide with sodium first order with respect to ethyl iodide. He assumed the presence of a "high stationary radical concentration" and discarded a view that the rate was controlled by diffusion of the iodide to the sodium surface, because the reaction of isopropyl iodide progressed much more slowly than would have been predicted from changes in the diffusion rates. If the coating on the metal surface has not been exactly the same in each case, as indeed seems doubtful, the necessity for assuming a special concentration of free radicals would be obviated.

The third specification is that the carbon-halogen bond should be sufficiently firm that the alkyl halide will not react too rapidly with the organosodium product. Exact information on this matter is lacking because the subject of reactivity is interwoven with that of penetrability of the surface coatings. Highest yields of monosodium compounds have been obtained with primary alkyl chlorides and with chlorobenzene; moderate to poor results with secondary and tertiary chlorides, with alkyl bromides and iodides.

Our opinion is that high yields are obtained when the carbon-chlorine bond is so unreactive that the alkylsodium can be pushed some distance from the metal before undergoing any appreciable reaction; that poor yields are found when the carbon-chlorine bond is so labile that the initial alkylsodium product reacts in the immediate vicinity of the metal surface and thus forms an adhering layer of sodium chloride. This view does much to explain the long existing anomaly that halides which react most readily with water are least reactive with sodium.

**Sodium Metal as a Trap.**—The suggestion has been made<sup>5</sup> that the mode of addition and the excess metal used in these preparations serve to trap the free radical as fast as formed. If so, the trap is perfect and there is again no need for assuming a free radical. But it is difficult to believe that these ideal conditions serve merely as a trap for a

(5) Richards, *Trans. Faraday Soc.*, **36**, 956 (1940).

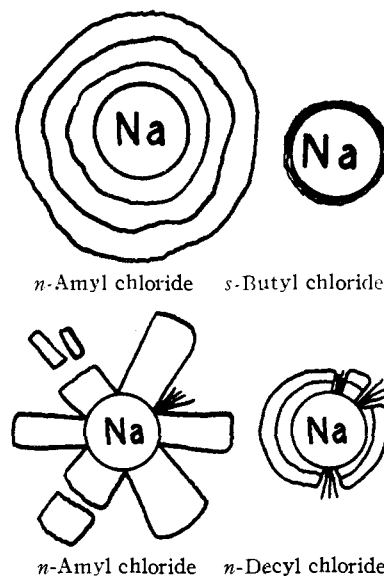


Fig. 1.—Sketches showing the appearance of small particles of metallic sodium when in contact with an alkyl chloride.

radical which might otherwise be free. The smallest particles we have yet prepared vary from 0.08 to 0.2 mm. in diameter.<sup>6</sup> One drop of alkyl chloride is more than enough to cover the surface of all such metal one molecule thick. Since addition of drops is regular, it would be no time at all before the coating would be appreciable. Certainly, there is no visual evidence that the metal surface is bright and shiny after the first few drops of alkyl chloride have been added; nor is there evidence under the microscope that any part of the metal is exposed. It seems unreasonable to suppose, therefore, that the metal surface beneath the coating on small particles is any more ideal for trapping than is that beneath the surface of very large particles. In both cases this coating must be traversed before the chloride makes contact with the metal. The rate of this diffusion is, therefore, important. The advantage of the finely divided metal reaches only to the point of affording enough surface of this type that the first phase can compete favorably with the second phase for the alkyl halide; not to the point of offering an unlimited area. This view is supported by two earlier experiments<sup>2</sup>; amyl chloride was added to fine sodium sand in one case, and the same sized sand was added to amyl chloride in the second. The yield of decane was approximately the same in each case.

It is, therefore, obvious that there is no phenome-

(6) Measurements by the courtesy of E. L. Little.

non whatever that requires or profits by assuming a free radical as a precursor of the organosodium compound. If any such radical exists the present methods of testing have not revealed it.

### Experiments

**Carbonation of *n*-Butylsodium (by H. N.).**—The apparatus was similar to that used in previous work. Sodium sand, 35 g. (1.5 g. atoms), activated by 2 ml. of isoamyl alcohol while stirred in 200 ml. of petroleum ether, was treated with 31.5 ml. (0.3 mole) of *n*-butyl chloride added dropwise with an equal volume of petroleum ether at 18–20° over a period of one hour. After being stirred for an additional hour, the mixture was forced from the flask under pressure of nitrogen onto solid carbon dioxide. The yield of valeric acid was 42.2% (0.126 mole); that of propylmalonic acid was 3.3%.

**Microscopic Examination of Coating Formed on Sodium (by J. D.).**—A small quantity of fine sodium sand was placed in the cavity of a hanging-drop microscope slide which contained *n*-decane. A cover glass was then placed so as to nearly close the cavity. The tip of a specially built micro-pipet was then inserted in the opening and small quantities of alkyl chloride pushed into the cavity by slowly turning a screw device on the far end of the pipet. Observations were made with *n*-propyl, *n*-butyl, *n*-amyl, *n*-octyl, *n*-decyl, cetyl, and *s*-butyl chlorides.

**Improved Conditions for Isolating the First Phase (by J. D.).**—The apparatus was an improved model of the high-speed stirring equipment described in an earlier paper.<sup>7</sup> A weighed amount (11.5 g. (0.5 atom)) of sodium metal was put in the flask and 340 ml. of *n*-octane added. The mixture was then heated to 105° at which temperature the stirrer was operated at 10,000 r. p. m. until the metal was finely dispersed, after which the stirrer was stopped and the flask allowed to cool. The powder prepared by this method settled slowly and was the finest which so far

(7) Morton and Knott, *Ind. Eng. Chem., Anal. Ed.*, **13**, 649 (1941).

has been obtained in this work. It required no activation by amyl alcohol.

*n*-Amyl chloride (30.2 ml. or 0.25 mole) diluted with 30 ml. of *n*-octane was added over a period of one hour during which time a bath of kerosene and solid carbon dioxide kept the temperature at 0°. After one additional hour of stirring (all at 10,000 r. p. m.) at this temperature, the reaction mixture was forced out of the container onto solid carbon dioxide by a pressure of nitrogen. The yield in two separate experiments was 71 and 72% total acids. The best yield previously obtained, using these proportions of reagents, was 63%. This improvement was realized in spite of adverse solvent conditions shown earlier<sup>8</sup> in this series.

Although these conditions are far better than any so far employed, they are still insufficient to give a high yield of organosodium compound from a secondary halide. Under comparable conditions, 2-chlorobutane and 2-chloropentane yielded 1.5 and 2.2% of acids, respectively.

### Summary

The first phase of the Wurtz reaction is reasonably interpreted as the formation of an organosodium intermediate.

Conditions necessary for preparing this intermediate in quantitative yield are described.

Primary halides form a loose porous coating in the surface of sodium. Secondary halides form a comparatively impenetrable coating.

The difficulties in separating the first from the second phases of the Wurtz reaction are discussed.

The function of finely divided sodium sand does not appear to be that of a trap for a free radical.

Assumption of a free radical is unnecessary.

(8) Morton and Palmer, *This Journal*, **60**, 1428 (1938).

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## Condensations by Sodium. XXIII. The General Theory of the Wurtz Reaction. Part II. The Second Phase

BY AVERY A. MORTON, JOHN B. DAVIDSON AND BARTON L. HAKAN

The previous paper<sup>1</sup> contained evidence that an organosodium compound could represent the first phase of the Wurtz reaction; this paper will show that the reactions of this intermediate with an alkyl or aryl chloride can constitute the concluding phase.

In the main the arguments for this thesis are: (1) disproportionation is a logical consequence of such a reaction; (2) polymerization proceeds

(1) Morton, Davidson and Newey, *This Journal*, **64**, 2240 (1942).

according to a regular pattern and products are predictable with an organometallic theory. It is further indicated that the phenomenon of metal-halogen interchange tends to obscure primary processes. Fluctuations in the products of the Wurtz reaction are shown to have no simple explanation on a free radical basis. A critical discussion of certain analogies from which a free radical mechanism for the Wurtz reaction has been inferred is presented.