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Condensations by Sodium. XXI. *n*-Octyl- and *n*-Decylsodium

BY AVERY A. MORTON, JOHN B. DAVIDSON AND ROBERT J. BEST

Propyl, butyl and amyl chlorides, condensed with sodium in petroleum ether, produce, respectively, some 10, 14 and 57% of total acids, the ratios of malonic to monobasic acids being 1.5, 1.3 and 0.3, and form alkylbenzenes to the extent of 43, 70 and 61%.¹ We have now carried out similar condensations with octyl and decyl chlorides, following the usual procedure.

***n*-Octylsodium (J. D.).**—The conventional² apparatus and process were used with 25 ml. (0.15 mole) of *n*-octyl chloride and 15 g. (0.65 g. atom) of fine sodium sand in 635 ml. of petroleum ether at -10° . Carbonation by bubbling carbon dioxide below the surface gave yields of pelargonic acid, *n*-heptylmalonic and *n*-hexadecane of 49% (11.7 g.), 15% (2.3 g.) and 7% (1.2 g.), respectively; while allowing it to drift over the surface of the mixture, following Gilman and Pacevitz,³ gave corresponding yields of 23, 26 and 6%, respectively. Separation of the mono- and di-carboxylic acids in these experiments could not be effected in the usual manner because the malonic acid was soluble in petroleum ether, particularly in the presence of the mono acid. The fatty acid was, therefore, steam-distilled and identified as pelargonic acid by its boiling point 250° (uncor.) (lit.⁴ 254°) and its *b*-bromophenacyl ester melting at 65.0 – 66.2° (lit.⁵ 68.5°). The heptylmalonic acid was identified by its melting point 94.8 – 95.2° (uncor.) (lit.⁶ 96.5 – 98°) and by its neutralization value.

The pink-colored octylsodium product in suspension in petroleum ether was centrifuged, the clear supernatant liquid separated and carbonated, but no acid was recovered after acidification and extraction with ether.

(1) Morton, Richardson and Hallowell, *THIS JOURNAL*, **63**, 327 (1941).

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

(3) Gilman and Pacevitz, *ibid.*, **62**, 1301 (1940).

(4) Deffet, *Bull. soc. chim. Belg.*, **40**, 388 (1931).

(5) Moses and Reid, *THIS JOURNAL*, **54**, 2101 (1932).

(6) Verkade and Coops, *Rec. trav. chim.*, **49**, 568 (1930).

Nonylbenzene (J. D.).—To 16 g. of sodium, suspended with stirring in 200 ml. of sulfur-free toluene at 72° , 25 ml. of alkyl chloride was added dropwise over a one-hour period. There was obtained 7.7 g. of nonylbenzene (51%); b. p. 280 – 281° ; α^{20} 1.485, which gave a *p*-sulfonamide derivative, m. p. 94.5 – 95° .⁷

***n*-Decylsodium (R. B.).**—Under the same conditions as above, the yield of undecylic acid was 28.4%; that of nonylmalonic acid was 2.3%. The melting points of the undecylic acid and of its *p*-bromophenacyl derivatives were 29.5° and 68.1° , respectively.⁸ The melting point of the nonylmalonic acid was 100.5 – 102.0° (uncor.); temperature of decarboxylation, 140° . It was only slightly soluble in water, very soluble in ether, neutralization equivalent, 116 (calcd. 115). One hour at 160° converted it to undecylic acid.

Undecylbenzene (R. B.).—To 15 g. of sodium in 500 ml. of sulfur-free toluene 60 g. of decyl chloride was added as above. There was obtained 25.3 g. (74%) of undecyl benzene; b. p. $296 \pm 1^{\circ}$; α^{20} 1.4824; mol. wt. by the Rast method 235, calculated 232; and *p*-sulfonamide derivative, m. p. 95.7 – 96.2 .

Anal. Calcd. for $C_{17}H_{29}O_2NS$: N, 4.5. Found: N, 4.6 and 4.7.

Attempted Alkylation of Benzene and Anisole (J.D.).—The quantities and procedure for addition of octyl chloride to toluene, but with replacement of the toluene by benzene or anisole, gave after carbonating only 0.2 g. of liquid boiling within the range for octylbenzene. The products from benzene: 11.7 g. (68%) of octane, 6.2 g. (33%) of benzoic acid and 130 mg. of triphenylcarbinol; from anisole, 6.5 g. of phenol and 1.1 g. of an impure yellow acid.

Discussion.—These results show that *n*-octyl- and *n*-decylsodium are formed in about the same quantities and have about the same properties

(7) Huntress and Autenrieth, *THIS JOURNAL*, **63**, 3446 (1941).

(8) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941.

as amylsodium.¹ 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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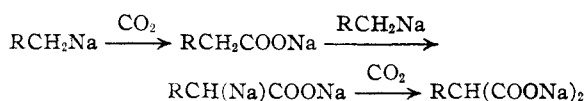
Condensations by Sodium. XXII. The General Theory of the Wurtz Reaction. The Initial Step

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

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,¹ 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.² Their results have been confirmed in this Laboratory, not only with amylsodium, but also with butylsodium which has shown³ 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 observed⁴ 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 work¹ 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).