tion 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.[7] 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[8] 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).

CAMBRIDGE, MASS.   RECEIVED MARCH 18, 1942

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 264]

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[1] 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.

Disproportionation.—Disproportionation has been so universally accepted as the criterion of a free radical that there has been no attempt to show a derivation from other molecular species.[1a] Nevertheless, a mechanism for this phenomenon by way of an organometallic intermediate appears exceptionally reasonable. If an alkylsodium meets an alkyl halide in such manner that the two alkyl chains are adjacent to each other while sodium halide is being formed, the two alkyl residues will have unlike charges and a proton will be drawn to the alkyl radical having the two unsaturated electrons. The reaction is merely the conventional prototropic change taking place between adjacent portions of two molecules whose inorganic components are effecting, or have just completed, a union.
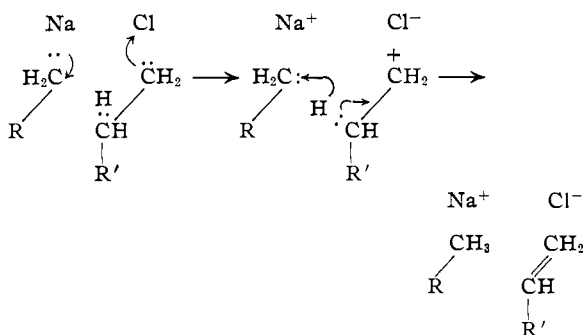
If this view be accepted, the olefin produced must come from the alkyl halide rather than at random from both participant alkyl radicals. Though conclusions are to some extent obscured by a metal–halogen interchange (see later), all available facts unquestionably point to the correctness of this deduction. In reactions which

TABLE I

PRODUCTS OF REACTION OF OCTYLSODIUM WITH ALKYL HALIDES

Halide	Per cent. yield of products			
	Octane	Octene	Hexa-decane	Wurtz product
Ethyl iodide	15.2	8.8	27.9	18.8
Ethyl bromide (V)[a]	14.6	10.3	10.7	31.0
Ethyl bromide	20.1	0.4	11.1	31.4
Ethyl chloride (V)	35.1	0.2	...	10.8
Propyl iodide	16.6	5.5	15.3	13.6
Propyl bromide	20.9	11.0	...	7.8
Propyl chloride	28.6	15.3	...	...

[a] The letter V refers to the fact that the reaction mixture became very viscous.

(1a) This statement was true at the time this article was submitted. Since then a paper by Whitmore and Zook has appeared (THIS JOURNAL, **64**, 1783 (1942)) in which the saturated and unsaturated products of disproportionation are credited as coming from the sodium alkyl and the alkyl chloride, respectively.

involved octylsodium and various alkyl halides (Table I), the octane predominated over the octene in every instance.

In parallel studies with amylsodium (Table II) the quantity of pentane in all cases exceeded the amount of pentene.

TABLE II

PRODUCTS[a] OF REACTION OF AMYLSODIUM WITH ALKYL HALIDES

Group	Halide	Pentane, %	Pentene, %	Ratio of pentane to pentene	Decane, %	Wurtz product
1	Methyl iodide	22.3	2.0	11.1	58.4	0
2	n-Hexyl iodide	5.4	5.0	1.1	39.8	32.6
	Methyl bromide	7.1	4.9	1.5	44.4	13.1
	Ethyl iodide	8.2	5.7	1.4	30.9	2.1
	n-Butyl iodide	7.8	6.3	1.2	30.4	17.8
3	Ethyl bromide	12.3	8.5	1.4	15.1	24.2
	n-Butyl bromide	13.1	11.4	1.2	10.0	32.0
	n-Hexyl bromide	9.8	8.5	1.2	15.2	45.6
	n-Hexyl chloride	5.1	1.6	3.2	19.8	13.4
	n-Butyl chloride	7.4	2.8	2.7	6.4	8.8
4	Ethyl chloride	11.6	1.1	11.1	9.0	30.2
	Methyl chloride	15.2	1.0	15.2	6.3	43.7

[a] The arrangement is in the approximate order of decreasing decane content in order to illustrate an important point developed later in this discussion.

A third series (Table III) compares (a) reactions between two radicals (amyl and hexyl) in which the inorganic components were interchanged and (b) reactions of hexylsodium with amyl and octyl chlorides which represent radicals smaller and larger than hexyl. The distribution of alkanes and alkenes was again not at random.

TABLE III

PRODUCTS FROM REACTION OF AMYL, HEXYL AND OCTYL RADICALS

| Reaction pair: RNa + R'Cl	Hexane, %	Hexene, %	Octane, %	Octene, %	Wurtz product, %
$C_5H_{11}Na + C_6H_{13}Cl$	9.5	11.5			24
$C_6H_{13}Na + C_5H_{11}Cl$	30.	7.7			23
$C_6H_{13}Na + C_8H_{17}Cl$	24.5	7	9.5	22.6	25

In these three series of experiments carried out under different conditions with widely different halides and various alkylsodium compounds, the products of disproportionation were uniformly proportioned according to the principle outlined above.

Polymerization.—A previous paper[2] recorded that the reaction of amylsodium with chlorobenzene produced more polymer than any other isolable product; that of phenylsodium with amyl chloride produced less polymer than any other

(2) Morton and Fallwell, *ibid.*, **60**, 1429 (1938).

fraction. The total quantity in the last case was about a fifth that obtained from the first pair of reactants.

The organometallic mechanism affords an adequate explanation for this polymerization. The disproportionation process between amylsodium and chlorobenzene leads to a dipolar phenylene as shown
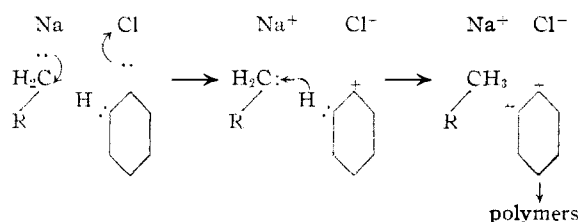
This intermediate dipolar compound cannot be stabilized by double bond formation and consequently undergoes further reaction with polar reagents. It may, for example, unite with more amylsodium giving a new organosodium compound which then reacts with more chlorobenzene according to a general scheme outlined
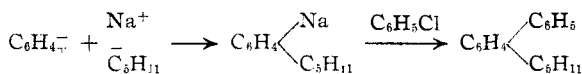

It may also condense with itself. The dimer would be a new dipolar intermediate which could react with more organosodium compound. The trimer could be the stable triphenylene. More complex products are obviously possible
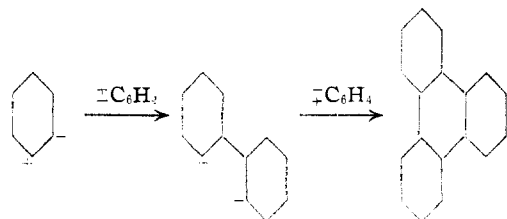
In any event, ortho substituted products should predominate, and the polymer should be composed of more radical from the halide than from the organosodium reagent. These conclusions are supported by facts. In the reaction of chlorobenzene with sodium,[3] the proportion of ortho to para substituted products was more than a thousand to one; in the reaction of amylsodium with chlorobenzene[2] one fraction contained three phenyl to one amyl unit. The triphenylene produced by reaction of chlorobenzene with sodium is thus a consequence of a series of changes by polar re-

agents rather than an indication that free radicals are at hand.

Metal–Halogen Interchange.—A metal–halogen interchange has been known for some time to occur between lithium alkyls and bromo- and iodo- compounds.[5] Since methyl iodide reacts with octyl- or amylsodium,[6] yielding hexadecane and decane, respectively, this process, too, may be associated with a preliminary formation of amyl iodide according to the equation

$$C_5H_{11}Na + CH_3I \longrightarrow C_5H_{11}I + CH_3Na$$
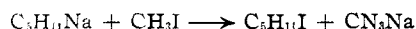
In agreement with this view, amyl iodide was obtained in 50% yield when amylsodium was added to methyl iodide. The comparative yields of hexadecane (Fig. 1) and of decane (Table II) suggest the extent to which this change occurs in other cases. Iodides in general appear to favor an interchange, and methyl iodide reacts preponderantly in this manner. Chlorides, on the other hand, with the possible exception of the hexyl compound seem to participate only slightly in exchange reactions.

When such an exchange occurs, the new products can then in turn undergo disproportionation or coupling. The results of such secondary reactions complicate seriously the effort to trace primary processes. Since disproportionation is then operating in the reverse order and some alkane is formed from what was originally the alkyl halide, this change is one factor which tends to lower the ratio of alkane to alkene. In any given case, a high yield of symmetrical coupling product would indicate a large amount of metal–halogen interchange and would be associated with a low ratio of alkane to alkene. Qualitatively, the results are in agreement with this view. n-Hexyl, n-butyl and ethyl iodides and methyl bromide (Table II) each formed decane in over 30% yield and gave a pentane–pentene ratio of from 1.1 to 1.5. On the other hand, the two lowest percentages of decane, viz., those obtained with methyl and ethyl chlorides are associated with the highest ratios. Methyl iodide alone appears anomalous. The majority of the bromides as well as n-butyl and hexyl chloride occupy an intermediate position in that the large amount of decane predicted

(3) Bachmann and Clarke, THIS JOURNAL, 49, 2092 (1927).

(4) (a) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, pp. 452, 537; (b) Hey, Annual Reports, 37, 245 (1941); (c) Richards, Trans. Faraday Soc., 36, 956 (1941); (d) Morton, Massengale and Richardson, THIS JOURNAL, 62, 126 (1940).

(5) Marvel, Hager and Coffman, ibid. 49, 2323 (1927); Wittig and Pöckels, Ber., 72, 89 (1939); Gilman and Banner, THIS JOURNAL, 62, 344 (1940).

(6) Morton and Fallwell, ibid., 59, 2387 (1937).

by a low pentane–pentene ratio appears to have been replaced by relatively higher proportions of Wurtz coupling products. The data in Table II are divided into four groups in order to indicate these relationships.

Variation of the Products.—A radical which is really free might be expected to show a specific chemical behavior toward another reagent irrespective of its source. That is to say, methyl, derived by reaction of the chloride, bromide or iodide with octylsodium, should have one reaction only with octyl, provided, of course, that the environment was constant and the concentration of the methyl radical was always so low that it could not react with itself. Figure 1 shows that such is not the case. Data in Tables II and III do not support this view. This argument may be questioned on the ground that the rate of formation of the methyl radical is different in the three cases. If the method of adding the methyl halide as a vapor in a stream of nitrogen does not keep the concentration sufficiently low, or if other changes are possible during the different periods of formation, then we would conclude that the rate should be fastest with the iodide and slowest with the chloride, and that a rapidly formed methyl radical would promote symmetrical coupling (hexadecane); a slowly formed radical would favor unsymmetrical coupling (nonane). These deductions from the free radical view, however, contribute nothing concrete to the explanation of phenomena in the Wurtz reaction compared with that offered by the organometallic theory.

Apart from considerations of mechanism, the results with the methyl halides are interesting because they show the limits possible in control of the products of the reaction.

Analogies with Other Reactions.—Before the general theory of the Wurtz reaction can be summarized in terms of organometallic compounds, some attention should be given to analogies which have suggested the likelihood of free radicals being the active agent. Polanyi[7] found good reason for postulating the existence of free methyl in reactions of methyl iodide with sodium vapor at extremely low pressures and comparatively high temperatures. The existence of free radicals under conditions highly favorable for their occurrence and above the limit of thermal stability of the alkylsodium compound is, of course, an entirely different matter from the assumption of

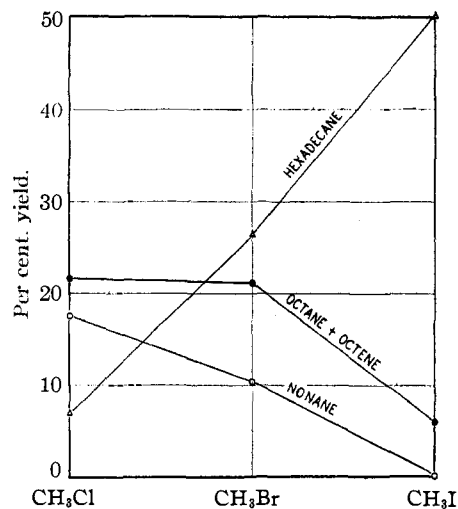(7) Horn, Polanyi and Style, Trans. Faraday Soc., **30**, 189 (1934).

Fig. 1.—Yield of products obtained by reaction of methyl halides with octylsodium.

their existence in a liquid phase at ordinary pressures on a surface of metallic sodium. Where even such ideal conditions as those mentioned have as yet failed to demonstrate the presence of free propyl, butyl and higher members[8] of the series, the conclusion might well be drawn that free radicals, so extremely difficult to obtain in an appropriate environment, would have little chance of being present in such an unfavorable medium as a liquid phase.
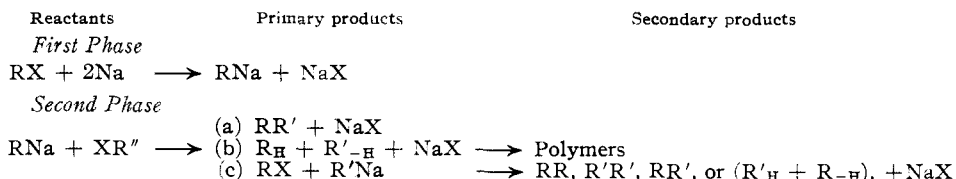
Another analogy stems from the vast amount of research on triphenylmethyl and other free radicals of long life. The reasoning in this case is very logical. If there are free radicals of long life, there should be also free radicals of short life. The force of this argument is granted; the opinion that any fact so far submitted definitely indicates their occurrence in the Wurtz reaction is questioned. Assumption of presence of a free radical in a system obviously containing a large proportion of an active polar compound implies that the two-step process involving, first, a change of ion to free radical and then a combination of radicals with themselves is faster than the direct interaction of ions to give the final product. There is no evidence so far available to support the idea that the ion is not itself sufficiently reactive without the interposition of a secondary change to a second intermediate of questionably greater activity. The converse indeed might well be true and the phenomenon of disproportionation which occurs in free radicals of long life, might be itself preceded

(8) Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, pp. 33, 64.

by conversion of the radical to an ion before a proton moves from one radical to the other.

General Summation of Reactions.—All primary and secondary products from the Wurtz reactions can be expressed by the following sets of equations

Reactants	Primary products	Secondary products
First Phase		
RX + 2Na $\longrightarrow$ RNa + NaX		
Second Phase		
	(a) RR' + NaX	
RNa + XR'' $\longrightarrow$	(b) $R_H + R'_{-H}$ + NaX $\longrightarrow$ Polymers	
	(c) RX + R'Na $\longrightarrow$ RR, R'R', RR', or $(R'_H + R_{-H})$, +NaX	

The relative importance of these various reactions differs with the reagents used. As far as the Wurtz coupling product, RR', is concerned, the yields decrease as the radical attached to sodium is benzyl, phenyl or alkyl. This order is the same as the relative affinities for sodium observed in metalation studies. As for the halide half of this reaction, the limited number of observations so far made suggest that bromides as a class are apt to give better results than iodides or chlorides.

The purpose of this work is not, of course, to deny all existence of a free radical in the Wurtz reaction but to point out that in the present state of knowledge on this subject the very phenomena for which the free radical interpretation has been considered essential in reality furnish excellent evidence that an organometallic agent is at work. In spite of very commendable efforts in the past, decisive evidence of any free radical phase which may be present in this common reaction is a goal yet to be reached. On the other hand, the organometallic mechanism is an adequate instrument for interpreting and predicting the reactions known to occur. It is, of course, beyond the scope of this paper to rewrite all equations of disproportionations in the Wurtz reaction which previously have been written as being in agreement with or supporting the free radical concept. It is sufficient to say that all such phenomena can be expressed satisfactorily as the normal behavior of a polar reagent, which has been proved to be present in sizable quantities.

Experiments

Octylsodium and Alkyl Halides (J. D.).—The apparatus consisted of a 500-ml. flask with four creases and an inverted bottom.[9] The usual three-necked addition tube was employed. The stirrer was operated at 1500 r. p. m. *n*-Octylsodium was prepared by adding 0.15 mole of octyl

chloride to 15 g. of sodium sand over a one-hour period at $-10°$, as described before.[1] Methyl, ethyl and propyl halides were then admitted by vaporizing them in a current of nitrogen while the liquid was kept about 10° below its boiling point. The tube between the vaporizer and the reaction vessel was electrically heated in order to prevent condensation of the vapors. The inlet tube terminated just above the surface of the suspension of octylsodium so as to ensure as far as possible a maximum opportunity for reaction of the alkyl halide with excess organosodium compound. One-tenth of a mole of each halide was added except in the case of methyl chloride, which being a gas, was allowed to pass slowly over the surface until reaction was complete. Water was then added to remove excess sodium. The hydrocarbons, RR', were fractionated through a column of the Podbielniak type having about ten theoretical plates, and collected over a 5° range. The octene content of the octane fraction (118–125°) was measured by a bromination method.[10] The hexadecane boiled from 277 to 283°. Percentage yields (Fig. 1 and Table I) are calculated on the basis of the octyl chloride used. For some undetermined reason the reaction mixture occasionally became so viscous that stirring was nearly impossible. The letter (V) in the table indicates when this condition was present.

Amylsodium and Alkyl Halides (J. D.).—The apparatus used in this series was the one mentioned before as operating at 10,000 r. p. m. Amylsodium was prepared by adding 30.2 ml. (0.25 mole) of *n*-amyl chloride to 11.5 g. (0.5 atom) of sodium powder during one hour at 0°. After the reaction mixture had been stirred for an additional hour, 0.177 mole of the alkyl halide was added dropwise at 0° during one-half hour. The mixture was stirred for fifteen minutes longer, then poured on solid carbon dioxide, and later treated with water to remove the very small amount of unreacted sodium metal. The hydrocarbon products were separated as in the foregoing description. Results are tabulated in Table II.

Amyl-, Hexyl- and Octylsodium with Alkyl Halides (B. H.).—The apparatus in this case was, in general, similar to that employed for octylsodium except that the stirrer was operated at 4000 r. p. m. The sodium sand (17.5 g.) was suspended in olefin-free pentane and activated by addition of 1.7 ml. of amyl alcohol. The alkyl halide (1 mole equivalent to 2 g. atoms of sodium metal) dissolved in twice its volume of pentane was added at 0 to $-5°$ over a one-hour period. The second alkyl halide (about 0.7 mole equivalent) was then added at the same rate. After stirring for a brief time longer, carbon dioxide was passed into the mixture to remove any unchanged organosodium compound which was always present in a small amount only, and water was added to remove excess sodium. The hydrocarbon layer was dried over calcium

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

(10) Uhrig and Levin, *ibid.,* **13**, 90 (1941).

chloride and then fractionated through a packed column having about twenty plates. Yields are given in Table III. Calculation is based on the quantity of alkyl halide added. The percentage yield of the Wurtz coupling product is determined on the basis of the first halide added. All results are the average of two determinations.

Amylsodium and Methyl Iodide (J. D.).—*n*-Amylsodium, prepared as in the previous experiment, was forced, during a fifteen-minute interval, into a flask containing 168 ml. of methyl iodide maintained at a temperature between −30 and 20°. After adding water to remove excess sodium, the organic layer was fractionated in the packed column at reduced pressure. The fraction boiling from 57 to 60° at 30 mm. had a specific gravity of 1.504 (recorded value[11] for amyl iodide 1.517) and weighed 23 g. (47% based on the amyl chloride used). The sodium fusion test for halogen was positive. The 3,5-dinitrobenzoate derivative, prepared from this fraction, melted at 44–45°. The recorded value[12] is 46°.

(11) Lieben and Rossi, *Ann.*, **159**, 74 (1871).

(12) Malone and Reid, THIS JOURNAL, **51**, 3426 (1929).

Summary

Complete explanations for the phenomena of disproportionation and polymerization, hitherto considered as demanding a free radical intermediate, are made on the basis of an organometallic reagent.

The saturated hydrocarbon product of disproportionation comes from the organosodium compound, the unsaturated from the halide.

Amylsodium yields amyl iodide when poured into methyl iodide.

The general basis from which a free radical theory is associated with the Wurtz reaction is critically discussed.

All products in the Wurtz reaction are interpreted on a simple basis by the organometallic mechanism.

Condensations by Sodium. XXIV. The Pyrolysis of Amylsodium

BY AVERY A. MORTON AND HERBERT A. NEWEY

The experiments reported in this paper are directed toward a careful examination of the stability of amylsodium over a wide range of temperature and toward a determination of the type of reaction involved in pyrolysis. The information was of importance to a general understanding of the behavior of amylsodium in various reactions and in particular to the studies on mechanism since an appreciable quantity of pentane or pentene formed by low temperature pyrolysis would nullify some of the conclusions drawn in the previous paper.[1] The products of pyrolysis proved clearly to be the result of metalation and dehydrogenation.

Pyrolysis required thirteen hours at 60° for completion and was fast enough at 120° and above to be observed by rapid evolution of gas. The rate of pyrolysis over a two-hour period was slight at 40°, moderate (22%) at 70°, and approximately complete at 90° (see Fig. 1). The slopes of the curve at 45, 55 and 65° are as 2.4 to 4.9 to 8.7. The logarithms of the reciprocal of these values, plotted against the temperature, give approximately a straight line. Extrapolation of this line to 20 and to 0° shows that the decomposition over

(1) Morton, Davidson and Hakan, THIS JOURNAL, **64**, 2242 (1942).

a two-hour period was definitely below 1% and probably negligible. Since the time period required for the experiments on the mechanism of the Wurtz reaction was considerably less than that employed in these pyrolysis experiments, there is no danger that the comparative quantities of pentane and pentene were affected by decomposition of the organosodium compound.
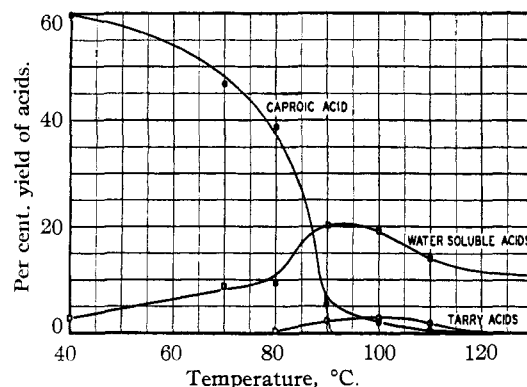

Fig. 1.—Yield of acids obtained after heating amylsodium for two hours at different temperatures.

The curve (Fig. 1) suggests that disappearance of amylsodium is related to appearance of another sodium compound which upon carbonation yields