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.
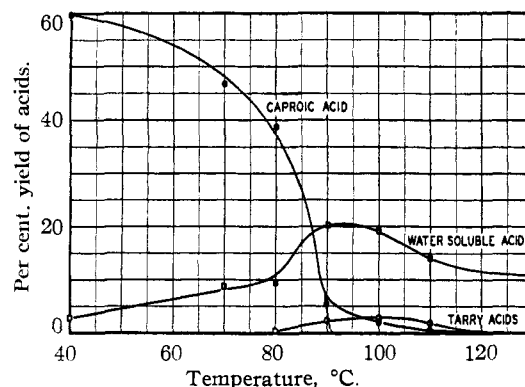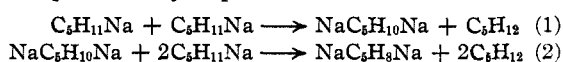

Fig. 1.—Yield of acids obtained after heating amylsodium for two hours at different temperatures.

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

very water-soluble carboxylic acids. At 90° the quantity of such acids was 20%. In view of the 60% yield of caproic acid before pyrolysis, it would appear that about one-third of the metal in amylsodium was present in the new compound. The remaining two-thirds had apparently reverted to sodium.

Examination of the acids, which were complex, showed more clearly the direction of the changes. Except for some tarry product, the acids which resulted from carbonation of the pyrolyzed organosodium compound had more than one carboxyl group per original amyl unit (in a preferred fraction nearly two such groups) and showed unsaturation. These changes in their elementary form are pictured by Eqs. 1 and 2.

$$C_5H_{11}Na + C_5H_{11}Na \longrightarrow NaC_5H_{10}Na + C_5H_{12} \quad (1)$$
$$NaC_5H_{10}Na + 2C_5H_{11}Na \longrightarrow NaC_5H_8Na + 2C_5H_{12} \quad (2)$$

The carboxyl groups are not attached to the same carbon atom, since tests on the preferred fraction showed no carbon dioxide evolution below 140°. Neither did the di-acid appear to form an anhydride when heated to 200°. These results suggested remote carbon atoms as points for attachment of sodium. Efforts to simplify identification of the product by hydrogenation failed to produce other than oily products. The possibility of some rearrangements occurring is not excluded, of course. The process of producing unsaturation, if continued a second time, would lead to a diene. Polymerization of such an unsaturated compound would account for the tars and other obviously large polymers produced.

No fragmentation of the carbon chain was evident since gases such as ethylene or propylene were not formed. The only gaseous product evolved was pentane with but a trace of pentene and this hydrocarbon was not evolved rapidly enough to be observed readily under the conditions employed until the temperature was above 120°, far above the point where, after longer periods of heating, the acidic products recovered showed obviously that pyrolysis had been complete.

All of the foregoing results are readily understandable as the behavior of an organosodium reagent without the necessity for assumption of any free radical. However, the mode of decomposition of all organosodium compounds under different conditions is not necessarily the same. For example, Carothers and Coffman,[2] who examined the gaseous products only of the pyrolysis

of ethylsodium in absence of any solvent, found that ethylene was the first gas evolved. These investigators assumed also that sodium hydride was formed. The present study showed that this last material was produced at relatively high temperatures and then only in small quantities. Formation of an alkane instead of an alkene as the principal hydrocarbon product of pyrolysis of amylsodium may be due to the longer alkyl chain, the end portion of which can apparently be metalated.

In previous papers,[3] efforts were made to improve the yield of butylmalonic acid by heating amylsodium before carbonation. Little or no increase resulted. These results are confirmed by the present work. The idea of an amylidene disodium is, in view of recent evidence that one amyl radical exists for every combined sodium, no longer tenable.[4] The approximate constancy of the butylmalonic acid noted previously must therefore be ascribed either to a difference in size and reactivity of the solid particles, a common occurrence indeed in these reactions, and to variations in the process of carbonation, which in the light of present knowledge would certainly produce some quantities of the dicarboxylic acid.

Experimental

Amylsodium was made in a creased flask in the usual manner[5] from 19 g. (0.82 g. atom) of sodium sand, 32 g. (0.3 mole) of n-amyl chloride, in olefin-free pentane (b. p. 30–40°). The metal was activated as usual with 2 ml. of isoamyl alcohol prior to addition of the chloride. Preparation was carried out at 10–15°, during one hour, and the mixture stirred for one hour longer at the same temperature. The pentane was then removed by distillation and 250 ml. of synthetic n-decane added. The mixture was then heated and stirred at the temperature desired for pyrolysis. Carbonation was effected by cooling the mixture to room temperature and forcing it under nitrogen pressure onto lumps of solid carbon dioxide.

After carbonation was complete, water was added to remove excess sodium metal and to dissolve the sodium salts. The aqueous layer was then acidified by hydrochloric acid. Tarry acids which separated were recovered by filtration or lifted out on a stirring rod, washed with water, dried, weighed and titrated. The aqueous layer was extracted with petroleum ether to remove caproic acid, which boiled between 202 and 206° and left little residue. This acid was further identified by conversion to the p-bromophenacyl ester melting at 72° (recorded value 72°). The quantity of acid was determined by titration and also by weighing the distillate. The remaining water-soluble

(2) Carothers and Coffman, THIS JOURNAL, 51, 588 (1929).

(3) Morton and Hechenbleikner, ibid., 58, 1697 (1936); Morton and Richardson, ibid., 62, 129 (1940).

(4) Morton, Davidson and Newey, ibid., 64, 2240 (1942); Gilman and Pacevitz, ibid., 62, 1301 (1940).

(5) Morton and Richardson, ibid., 62, 123 (1940).

Table I

Properties of the Methyl Esters of the Acids Produced by Carbonation of the Product of Pyrolysis of Amylsodium at Temperatures from 80–130°

Frac.	B. p., °C.	B. p., °C. 760 mm.	Quantity, g.	S. E.[a]	Carbomethoxy groups per amyl unit	Mol. wt. Calcd.[b]	Mol. wt. Obs.[c]	Polymer in amyl units	Double bonds[d]
1[e]	80 (20 mm.)	205	0.5	112	1.32	148	196	1.3	+
2[f]	110–120 (5 microns)	285	2.5	98[g]	1.80	176	197	1.1	1.15
3	120–250 (5 microns)	...	0.3	101	1.67	168	268	1.6	+
4	Residue		6.7	135	.92	124	900	7.3	+

[a] Saponification equivalent. [b] Average molecular weight per amyl unit calculated from the saponification equivalent. [c] Determined by boiling point elevation in acetone in a Swietoslawski apparatus. [d] Each fraction showed unsaturation. One fraction analyzed by catalytic absorption of hydrogen. [e] This fraction probably consists chiefly of methyl butylmalonate. [f] This fraction was considered as a preferred one because it was the lowest boiling of the pyrolyzed products and was the nearest to having two carbomethoxy groups to one amyl chain. [g] Neutralization equivalent of the free acid was 87 as determined by the silver salt.

acids were recovered by saturating the solution with salt and extracting first with ether and then with methyl ethyl ketone. The ether occasionally removed some butylmalonic acid which crystallized, but for the most part the products were extracted only by methyl ethyl ketone and remained as oily liquids after evaporation of that solvent. The results are given in the graph (Fig. 1). All yields are based on the amount of amyl chloride originally added.

A parallel series of experiments was made in which all conditions were the same except that carbonation was effected by bubbling carbon dioxide into the reaction mixture. The results are in general identical save for the formation of larger quantities of butylmalonic acid and the initial occurrence of tar at 68° instead of 80°. The data are therefore not recorded in this paper.

Acidic Products of Pyrolysis.—In general, the water-soluble products were dark brown, viscous materials slightly soluble in ether but readily soluble in methyl ethyl ketone, acetone or alcohol. In the case of the products of pyrolysis at temperatures below 90°, the recovered water-soluble acids could again be redissolved in water readily. Where the pyrolysis had been effected at higher temperatures the dried acid would not redissolve in cold water. A quantity of these acids from pyrolysis at 80 to 100° was esterified with diazomethane. Ten grams of the ester was distilled. The properties of each fraction are recorded in Table I. Although the second fraction was the one most likely to give a single compound, no crystalline ester or derivative could be obtained, even after catalytically hydrogenating, converting to the acid, amide, or p-bromophenacyl ester.

The tarry acids recovered from the low temperature pyrolysis were dark brown and sticky materials. As the temperature of pyrolysis increased, they became progressively harder and eventually appeared as a dry fluffy powder. These last products did not dissolve in acetone and formed a methyl ester which was not volatile in a molecular still. Hence their molecular weight was very high. The graph indicates a decrease in the tar formed at higher temperature. Actually the weight of the tar in that range remained fairly constant, the seeming drop being due to a loss in the number of carboxyl groups.

Formic acid, suggesting the presence of sodium hydride, was present in small amounts only and then only among the products of pyrolysis at higher temperatures. Detection was difficult. The method of proving its presence was to evaporate the combined sodium salts of the acids to dryness, add them to glacial acetic acid and fractionate carefully. A sample from the first portion of distillate readily reduced alkaline permanganate. Another sample was diluted with water, the aqueous solution treated with magnesium turnings and the resulting aldehyde[6] treated with dimethyldihydroresorcinol. The dimethone derivative, after being recrystallized, melted at 188–189° and showed no depression when melted with an authentic sample. Although other tests such as steam distillation of the water-soluble acids and treatment of the distillate with potassium permanganate or mercuric chloride showed evidence of its presence, the quantity of formic acid was never more than a trace. In fact, no conclusive evidence could be found that it resulted when the temperature of pyrolysis was kept below 90°.

Hydrocarbon Products from Pyrolysis.—The amylsodium was prepared as before, petroleum ether solvent removed, and n-decane added. On heating rapidly, a small amount only of material distilled from the mixture below 120°. No gases were evolved. Between 120 and 130° the mixture in the flask boiled vigorously. The condensate was collected in a trap which was cooled by solid carbon dioxide. All exit gases passed through a second trap containing bromine water. No decoloration occurred. The liquid caught in the first trap boiled between 34 and 40°, most of it at 34 to 36°, suggesting that the product was chiefly n-pentane. It decolorized only traces of bromine. On treatment with cold concentrated sulfuric acid less than a fifteenth of the volume was lost. The total volume of liquid collected was 33 ml., which was more than the amount equivalent to the amyl chloride used. The excess might have come from occlusion of some solvent used in preparation or from a complex formation of solvent pentane with amylsodium.

The contents of the reaction vessel, after pyrolysis, were poured on solid carbon dioxide, water was added, and the hydrocarbon layer collected and distilled. This material proved to be n-decane which boiled from 172 to 176°, and showed no unsaturation when tested by permanganate. The residue from fractionation contained no high-boiling compounds.

Summary

The rate of decomposition of amylsodium is

(6) Fenton and Sisson, Chem. Centr., 79, 1379 (1908).

very slight at 40°, fair at 70° and rapid (two hours for completion) at 90°.

Acids, obtained by carbonation of the pyrolyzed organosodium compound, are (a) water soluble, unsaturated compounds with more than one carboxyl group to amyl unit; (b) tarry or insoluble acids which are unsaturated and of relatively high molecular weight.

The sole hydrocarbon product was pentane. The solvent, n-decane, was not attacked by the organosodium compound under the conditions employed.

The chemical reactions which occur during pyrolysis involve metalation (dismutation) and dehydrogenation.

CAMBRIDGE, MASS.   RECEIVED MARCH 18, 1942

Condensations by Sodium. XXV. Reactions of Amylsodium with Naphthalene, Acenaphthene and Decalin

BY AVERY A. MORTON, JOHN B. DAVIDSON, T. R. P. GIBB, JR., ERNEST L. LITTLE, E. F. CLARKE AND A. G. GREEN

Nearly half of the carbonated product obtained from the reaction of amylsodium with naphthalene is di- and tri-substituted, whereas nearly all of the product in the case of benzene is monosubstituted. Octyl- is more active with naphthalene than is amylsodium and the proportion of higher substituted compounds is slightly increased. The α- and β-monoacids, and the 1,3-, 1,8-, and 2,6-dicarboxylic acids were isolated. The trisubstituted compounds were not examined.

Acenaphthene was expected to behave somewhat similarly to toluene. One sodium atom did, in fact, replace a hydrogen atom in a methylene group but a second one entered the ring, giving a dicarboxylic acid, probably the 1,5-compound, in about 50% yield. Oxidation of this diacid with permanganate gave 1,4,5-naphthalene tricarboxylic acid, showing that one carboxyl must have been attached to a methylene, i. e., in the
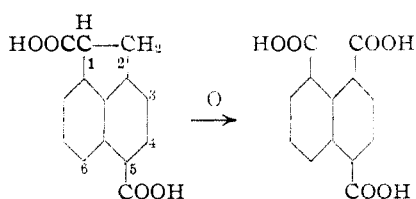
1-position, and the second was bound to the 5- or 6-position in the aromatic nucleus. The 5-position is considered more likely because (a) in benzene[1] the directing influence of one sodium atom on a second entering one is largely meta; (b) in naphthalene the influence on substitution of another metal in the same ring is meta; and

(c) even in benzylsodium[2] a second metalation, when it does occur, is exclusively in the meta position. The 5-position is also in accord with the general principle[3] that the introduction of substituents into a bicyclic system containing a meta directing group will take place in the unsubstituted ring. Metalation of acenaphthene by an organo alkali compound, butyllithium, has been observed[4a] once before but no product was isolated. Horvitz[4b] also studied the action of amylsodium on acenaphthene but was unable to obtain a product of known purity because of the difficulty in separation.

The action of amylsodium on decalin was most surprising because metalation took place with extreme ease. From a great variety of products a very small amount of a crystalline ester of a tetracarboxylic acid was eventually isolated. It readily formed a dianhydride after being saponified and acidified. The positions of the carbethoxy group are not known but the 1,4,5,8-product is suspected because these positions are reasonably remote from each other, and have the symmetrical arrangement which would increase the tendency of the compound to come out of mixtures in a crystalline form. Moreover, the corresponding acids could easily form a dianhydride of high melting point. The original hope had been that substitution would occur at the tertiary or indented position and that the process would therefore prove to be a new synthetical method in that

(1) Morton and Fallwell, THIS JOURNAL, **60**, 1924 (1938).

(2) Unpublished research.

(3) Grieve and Hey, J. Chem. Soc., 968 (1933).

(4) (a) Gilman and Bebb, THIS JOURNAL, **61**, 109 (1939); (b) Horvitz, Ph.D. Thesis, Massachusetts Institute of Technology, 1938.