

and a half hour period. Carbonation yielded no acids. The hydrocarbon layer was washed and fractionated at atmospheric pressure until nothing more would come over with the jacket temperature of the column at 186°. At 10 mm. pressure 11 ml. of material boiling from 98 to 112° and obviously containing some diphenyl, along with the hoped for cyclohexylbenzene, was obtained. This fraction was nitrated according to the procedure of Kursanoff,⁹ in an attempt to obtain the 4-nitrocyclohexylbenzene, m. p. 57.5–58.5°. The only products obtained were apparently higher melting nitro derivatives of diphenyl for the crude material melted 71–95°, and after crystallization from dilute acetic acid at 90–98°. Sublimation did not change the value appreciably.

Unsatisfactory results were likewise obtained in the reaction of this dibromide with amylienedisodium, the latter being made from 63.9 g. of amyl chloride with 37 g. of sodium in 300 ml. of petroleum ether in the usual manner. The dibromide, 36 g., was added dropwise. Carbonation produced no acids. Upon fractionation 9 ml. boiling 161–172° at atmospheric pressure was collected. It contained some decane as well as some of the expected *n*-butylcyclohexane. Hydrogen sulfide was evolved when the fraction was heated with sulfur but no evidence of *n*-butylbenzene could be obtained on applying Ipatieff's¹⁰

procedure for making the diacetamino derivative.

Summary

Ethylidene chloride reacts with amylienedisodium to form heptene-2. The yield is the same within the experimental error as that of butylmalonic acid obtained by carbonation.

Methylene chloride and ethylidene chloride react with benzylidenedisodium, yielding styrene and methylstyrene, respectively.

Styrene is not obtained from the reaction of β -phenylethyl chloride with benzylsodium.

Phenylsodium prepared from chlorobenzene is not as active in exchanges with toluene as is phenylsodium prepared from amylosodium.

Methyl iodide and dimethyl sulfate give approximately the same yields of ethylbenzene when added to the mixture of benzylsodium and benzylidenedisodium. In neither case is the branched chain hydrocarbon, isopropylbenzene, found among the products.

(9) Kursanoff, *Ann.*, **318**, 321 (1901).

(10) Ipatieff and Schmerling, *THIS JOURNAL*, **59**, 1056 (1937).

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Condensations by Sodium. XVI. The Formation of Decane in the Wurtz Reaction

BY AVERY A. MORTON AND GRAHAM M. RICHARDSON

It is the purpose of this work to show that no Wurtz product, decane, is formed until after formation of organosodium compounds. In brief, free radicals, if formed prior to organosodium intermediates by reaction of amyl chloride and sodium, do not dimerize to yield decane. The method employed was the simple one of increasing the quantity of sodium and noting whether the yield of organosodium compounds approached 100% as that of decane fell to zero. Such an examination of the early stages of addition of amyl chloride to sodium showed (Fig. 1) that yields were essentially quantitative, as high as 95% total organosodium compounds (amylsodium and amylienedisodium) being revealed by carbonation. This Wurtz reaction is therefore sharply divisible into two phases: first, the formation of organosodium compounds and, second, their reaction with alkyl chloride. Decane was exclusively a product of the second stage. Under certain conditions the yield of decane was as high

as 90% with respect to the monosodium compound.

At one time or another presence of free radicals has been proposed for nearly every stage of the Wurtz reaction. One argument for their existence is the finding of products of disproportionation, in this instance, pentane and pentene. Because of the prevalence of the free radical view and the failure of alternative mechanisms to prove satisfactory, presence of amylienedisodium (butylmalonic acid) was attributed¹ to occurrence of this active intermediate. Such a mechanism is in full accord with present notions of free radicals in solution and their behavior. Yet critical questions can be asked. Why, for example, should disproportionation occur when the free energies of the products unquestionably favor dimerization? Thus, in the case of ethyl reacting with itself to form ethylene and ethane or butane

(1) Morton and Hechenbleikner, *THIS JOURNAL*, **58**, 2599 (1936); Morton, Fallwell, and Palmer, *ibid.*, **60**, 1426 (1938).

the free energies² are +12,300, -10,700, and -6200, respectively. Data for trimethylethylene (+13,700), pentane (-8600), and decane (-2900) suggest that the same relations exist for the products in the reaction of amyl chloride and sodium. If heats of formation of bonds are considered, a greater amount of heat would be evolved for dimerization than for disproportionation. By applying Rice's³ method of calculating the probable proportion of products, the amount of disproportionation should be trifling. It is indeed an interesting fact that alkyl disproportionation, universally considered as evidence for free radicals, should not occur according to this single aspect of thermodynamics.

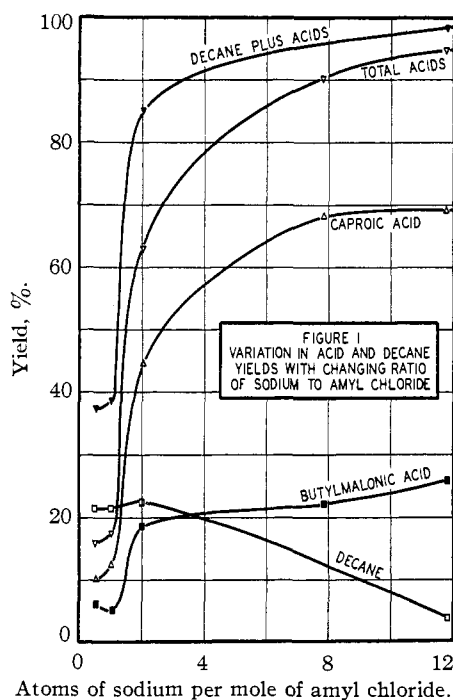


Fig. 1.—Variation in acid and decane yields with changing ratio of sodium to amyl chloride.

Furthermore, if free radicals are present in the first phase of reaction between amyl chloride and sodium and they react with sodium to form amylsodium or disproportionate to an -idene radical which in turn adds two atoms of sodium, one must concede that metallic sodium has acted as a nearly perfect trap for this radical or its disproportionated product. Yet how free can a

(2) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Johns Hopkins Press, Baltimore, Md., 1935.

(3) Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

free radical be which never escapes the influence of the surface of a metal on which it is formed and how can such a radical be distinguished from a radical in a complex, evidences of which are not entirely lacking in these reactions? Far more serious is the question of why disproportionation should be the sole product of reaction of a free radical with itself on the metal surface when free energies so overwhelmingly favor decane formation.

Our present opinion of the Wurtz reaction can be stated briefly. The Wurtz product, *i. e.*, the dimer, is reached by way of an intermediate organometallic compound. There is no need for any other special mechanism, although it is possible to superimpose on this view an ionic (organosodium compounds are salts) or a free radical mechanism. Owing to the vigor of the reactants and of the organosodium reagent, simultaneous side reactions and decompositions may occur to subordinate the Wurtz synthesis. Assumption of an intermediate free radical provides at present a convenient explanation for some of these products. This suggestion, while in general accord with current notions, requires further clarification before it can be unqualifiedly accepted. Certainly, at present, the evidence for such an intermediate is no better than that for a radical within a complex.

Experiments

General Conditions.—The general method described in previous papers was employed but owing to the purpose of the work special attention was paid to a number of factors having to do with increased yields. Sodium sand was made in pound lots in a special 1-liter flask⁴ in which stirring was more effective. The particles were about one-fourth the size of those formerly obtained. The reactions themselves were carried out in similar flasks which before alteration had a capacity of 500 ml. The quantity of amyl alcohol needed to activate 30 g. of sodium metal was found to be 2 ml. by the following series of experiments. Amyl chloride, 20 ml., in 40 ml. of benzene was dropped onto 30 g. of sodium in a mixed solvent of 80 ml. of benzene and 25 ml. of petroleum ether under an atmosphere of nitrogen at 0 to -4° over a period of one hour. The mixture was then stirred for two hours at room temperature, more of the solvent mixture being added if necessary, before carbonation at 22-28°. Yields of total acids were 82, 88, 84, 76, and 73% when the amounts of alcohol used to activate the metal were 0, 2, 4, 6, and 8 ml., respectively. At room temperature amylsodium was converted to phenylsodium but amyldenedisodium was largely unaffected so that yields of different acids in this series were, respectively: for benzoic acid, 72, 83, 62, 71, and 64%

(4) Morton, *Ind. Eng. Chem., Anal. Ed.*, **11**, 170 (1939).

(14.6, 15.4, 12.7, 14.2 and 13 g.); for butylmalonic acid, 9.5, 5.0, 22.5, 5.0, and 8% (1.3, 0.7, 3, 0.7, and 1.0 g.). Total yields of all acids showed a definite drop when large quantities of alcohol were used but the respective amounts of benzoic and butylmalonic acid varied once (with 4 ml.) in an unpredictable manner. In general loss of monosodium compound was greater.

Purifying nitrogen by passing it over heated copper, through sulfuric acid, and then finally through a preliminary reaction mixture to ensure thorough scrubbing showed little, if any, difference from results obtained with no gas purification. Thus under conditions identical with those described in the preceding paragraph except that 4 ml. of amyl alcohol was used to activate the sodium, yields of 16.3 g. (81%) of benzoic acid and 0.8 g. (6%) of butylmalonic acid were obtained. The total yield of 87% was only slightly higher than the corresponding value of 84% reported above. The purified and dried nitrogen had been allowed to bubble slowly through the pre-reaction scrubber which contained double the quantity of amylsodium for a total time of twenty hours. After carbonating and decomposing the contents of this scrubber in the usual manner there was found 29.5 g. (73%) of benzoic acid and 1.2 g. (5%) of butylmalonic acid (total 78%). No nitrogen-containing compound could be observed among the products. In all other experiments reported in this paper no attempt was made to purify the commercial nitrogen being used as the inert atmosphere.

Effect of Varying the Quantity of Sodium.—Amyl chloride, 20 ml. (0.17 mole), dissolved in 40 ml. of petroleum ether was dropped onto varying amounts of sodium sand suspended in 120 ml. of petroleum ether. The amyl alcohol used to activate the sodium was in the proportion of 2 ml. of alcohol to 30 g. of metal. The temperature was maintained at -15 to -20° throughout the one hour needed for addition, the thirty minutes required for agitation, and the time for carbonation. Usually it was unnecessary to add more solvent to facilitate stirring. At this low temperature elimination of side reactions such as decomposition of amylsodium, or metallation of sodium caproate during carbonation was expected. With 2, 4, 7.6, 30 and 45 g. (0.5, 1, 2, 7.9 and 11.8 ratio of atoms of sodium to moles of amyl chloride) of sodium the yields of total acids were 16, 17, 63, 90 and 95%, respectively, distributed between caproic 10, 12, 44, 68, and 69% (1.1, 2.4, 8.5, 13.1, and 13.2 g.) and butylmalonic acid 6, 5, 19, 22, and 26% (0.4, 0.7, 2.4, 2.9, and 3.4 g.). Decane was determined by fractionation, 40 ml. of Nujol being added in order to have a high boiling residue in the flask. In a test run, 10 ml. out of 10 ml. of decane was recovered in this manner. Corresponding yields of decane in the above series were 21, 21, 22, —, 3.8% (1.4, 2.51, 2.62, —, 0.44 g.). The blank space represents failure to estimate decane accurately because the Nujol method had not been developed at that time. The remainder of the product was a little high boiling residue but largely pentane and pentene, determined by difference. Results are shown graphically in Fig. 1. Attention is called to the stability of amylsodium under these conditions which even in the presence of excess amyl chloride (experiments with 0.5 atom of sodium to a mole equivalent of amyl chloride) failed to react completely. From this experiment 45%

(7.9 g.) of unreacted amyl chloride was recovered. From all other experiments no such halide fraction was found. Another interesting fact is that the ratio of percentage yields of butylmalonic to caproic acid did not vary greatly in this series, being 0.6, 0.4, 0.4, 0.3, 0.4, respectively. These data are in accord with the view that the disodium compound is not a secondary product of amylsodium.

Effect of Benzene and Petroleum Ether Mixtures.—This series of experiments was made in expectation that yields of organosodium compounds might be higher if the alkyl- were converted to the relatively inactive phenylsodium. The series showed, however, that amylsodium did not react with benzene below 0° and that the use of a mixed solvent had little effect on the yields of organometallic reagents. Results from typical experiments are shown in Table I.

TABLE I

EXPERIMENTS IN MIXTURES OF PETROLEUM ETHER AND BENZENE AS SOLVENTS

Constant factors: sodium 30 g. in a mixture of benzene and petroleum ether, amyl alcohol 4 ml., amyl chloride 20 ml. in 40 ml. of benzene; addition temp. -0 to -4° , addition time one and one-half hours, stirring temperature 27° , stirring time two hours, carbonation at room temp.

Benzene-petroleum ether mixture		Carbonation products				Total, %
Benzene, ml.	Petroleum ether, ml.	Benzoic G.	%	Butylmalonic G.	%	
80	50	11.5	57	3	23	79
80	25	12.7	62	3	22	84
80	10	12.4	61	3	22	83
80	5	10.0	49 ^a	1.5	11	60
80	25	10.5	54 ^b	3	24	78

^a Owing to the small amount of petroleum ether present, the benzene crystallized from the solution and prevented uniform stirring. ^b Caproic rather than benzoic acid because the temperature of stirring and carbonation was 0 to -4° . Amyl alcohol, 2 ml., used for activation.

Attention is called to (a) the lower yields in this series as compared with the one (90%) just previous, possibly because of the higher temperature at which these runs were made, (b) the constancy of the values for butylmalonic acid which were approximately the same as that in petroleum ether alone (22%) at -15 to -20° and which remained practically unchanged in the last experiment when carbonation was carried out at 0 to -4° , (c) the comparative inactivity of amylidenedisodium which did not react with benzene under these conditions, although amylsodium was entirely changed.

Decane.—The following experiments were made in order to see whether the yield of decane could be made approximately quantitative with respect to the amylsodium. Amylsodium was prepared from 20 ml. of amyl chloride and 2 atom equivalents (8 g.) of sodium sand according to the method used in studying the effect of varying the quantity of sodium. After the customary half hour of stirring at -15° the mixture was warmed to 30° and an additional lot of 20 ml. of amyl chloride added over a period of thirty minutes. The mixture was stirred for a half hour longer, carbonated and decomposed.

Caproic acid, 0.24 g. (0.6%), and butylmalonic acid, 0.17 g., were obtained. On fractionation 6.2 g. of amyl chloride and 7.6 g. of decane were recovered. The decane amounted to 40% of the amyl chloride actually consumed. The yield when the same experiment was carried out at -15° amounted to only 21%.

In the same apparatus with the same quantities of material but with the sodium being added to a solution of amyl chloride at 30° rather than amyl chloride to sodium, the yield of decane was 10 g. (41%). This last experiment was prompted by the idea that excess amyl chloride might act as a trap for amylsodium and thereby show whether the initial phase of the reaction were yielding a larger amount of amylsodium than was being obtained by the usual method. The decane formed, however, did not exceed the amount of amylsodium (44%) revealed by carbonation experiments.

High-boiling Compounds.—In order to see whether part of the amylsodium had been consumed during carbonation to form triamylcarbinol or other oxygen-containing substances, the non-acid products from eleven runs in petroleum ether as a solvent were combined and fractionated. The quantity represented was a total of 285 g. of amyl chloride, 430 g. of sodium activated by 41 g. of amyl alcohol from which 143 g. (46%) of caproic acid, 57 g. (27%) of butylmalonic acid, had been recovered. After removing 1 ml. of low-boiling material, 8.7 ml. of *n*-amyl alcohol and 24 ml. of decane, the residue consisting of 17 g. (only 7% of the total amyl chloride) was fractionated at 2 ml. pressure through an 8-plate column of the Podbielniak type. Six cuts were made from 44 to 114° but carbon (85%) and hydrogen (15%) determinations showed that no oxygen was present. A final residue of 2.5 g. was fractionated at 1 mm. in the apparatus of Peakes⁵ yielding 1 g. at 110 – 130° , 0.5 g. at 130 – 170° and 0.6 g. at 170 – 230° . This last fraction contained 3% of oxygen and was the only one found not to be entirely a hydrocarbon. All fractions showed a positive test for unsaturation with permanganate.

(5) Peakes, Jr., *Mikrochemie*, **18**, 100 (1935).

In the case of experiments in benzene, however, there was evidence of considerable oxygen-containing material. From thirteen separate experiments made in mixtures of petroleum ether and benzene involving a total of 280 ml. of amyl chloride, 420 g. of sodium and 58 ml. of amyl alcohol for activation, there was obtained a grand total of 164 g. (58%) of benzoic acid, 21 g. (6%) of butylmalonic acid and 11 g. (4%) of caproic acid, this last material coming from one run listed in Table I in which the temperature of carbonation was kept at 0 to -4° . The non-acidic portions from these experiments were combined and the benzene and petroleum ether removed by distillation. Triphenylcarbinol, 4.4 g. (0.7%), crystallized from the residue and was identified by its melting point and mixed melting point with an authentic sample. The remaining 35 g. of residue was stripped of about 12 g. of amyl alcohol and decane and then fractionated at reduced pressures. The oxygen content of this high-boiling material changed from an initial zero value to 3.9% for the last fraction. This oxygen was apparently not due to triphenylcarbinol since no further quantity could be separated from these portions.

Summary

No decane is formed prior to formation of amylsodium in the reaction between amyl chloride and sodium.

This Wurtz synthesis is divided into two distinct phases, that concerned with formation of the organometallic compound and that related to reaction of this intermediate with addition of alkyl chloride.

If free radicals are present in the early phase, their activity is limited to addition with sodium or to disproportionation and combination of the *-idene* product with two atoms of sodium to form another organometallic compound.

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Condensations by Sodium. XVII. Comments on the Formation of Triphenylene

BY AVERY A. MORTON, JOHN T. MASSENGALE AND GRAHAM M. RICHARDSON

In an excellent paper by Bachmann and Clarke,¹ presence of around 2.0% of triphenylene among the products of the reaction of chlorobenzene and sodium was noted. Lately, Blum-Bergmann² has reported small quantities of the same compound from the reaction of phenylsodium and bromobenzene thus showing that this substance can arise from the second stage of a

Wurtz synthesis. The importance of this material is that its formation is one of the major arguments for a free radical mechanism in Wurtz reactions, Bachmann and Clarke regarding its presence "among the reaction products as decisive in favor of the free radical explanation." In this paper we shall record the inadequacy of two other possible mechanisms not considered by the original investigators.

The first alternative is that *o*-phenylbiphenyl

(1) Bachmann and Clarke, *THIS JOURNAL*, **49**, 2089 (1927).

(2) Blum-Bergmann, *ibid.*, **60**, 1999 (1938).