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Condensations by Sodium. XV. Reactions of Disodium Compounds with Ethylidene and Methylene Chlorides[*]

BY AVERY A. MORTON AND JOHN T. MASSENGALE

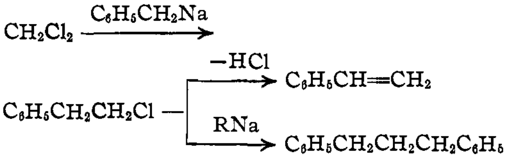
Amylidenedisodium has failed[1] to give branched chain hydrocarbons with monohalogen alkyls. However, reaction with ethylidene chloride is now shown to take place smoothly with formation of the expected heptene-2 (equation 1) in a yield of

$$C_4H_8CHNa_2 + Cl_2CHCH_3 \longrightarrow C_4H_9CH{=}CHCH_3 + 2NaCl \quad (1)$$

13%, or 80% of the maximum possible (17%) estimated from the butylmalonic acid usually obtained by carbonation. This compound is the first Wurtz product from disodium compounds reported in this work. Its isolation in the quantity noted is in agreement with the view that amylidenedisodium is present as an intermediate[2] from which butylmalonic acid is derived by carbonation.

Efforts to use this reaction for showing the existence of some benzylidenedisodium along with benzylsodium as a product of the exchange reaction between phenylsodium and toluene were qualitatively successful. Styrene from methylene chloride and methylstyrene from ethylidene chloride were both formed though the yield (not over 4%) did not exceed a quarter of that expected. It will be recalled[2] that a secondary reaction made estimation of this disodium intermediate by carbonation unreliable. Accordingly, an indirect method was used. Benzylsodium was first determined by measuring the amount of ethylbenzene produced with methyl iodide and with methyl sulfate. These values are in approximate agreement (46 and 43%, respectively) with each other and are considered a fair index of the quantity of benzylsodium since reactions of this organosodium compound have so far been among the most quantitative[3] with respect to the Wurtz product observed in this series. The difference between the total organosodium intermediates found by carbonation and the mono product approximated by the above method amounts to around 15%. Low yields of styrene may be due to difficulties in isolating the product as well as to poor reaction. Efforts to increase the styrene yield by heating benzylsodium with excess phenylsodium led to inactivation of the latter.

On the supposition that styrene might come by splitting out of hydrochloric acid from another likely intermediate (equation 2), beta-phenylethyl chloride, addition of the latter instead of methylene chloride was tried. No trace of styrene could be observed.



$$CH_2Cl_2 \xrightarrow{C_6H_5CH_2Na} C_6H_5CH_2CH_2Cl \begin{cases} \xrightarrow{-HCl} C_6H_5CH{=}CH_2 \\ \xrightarrow{RNa} C_6H_5CH_2CH_2CH_2C_6H_5 \end{cases} \quad (2)$$

Chlorobenzene instead of amyl chloride was used as a source of phenylsodium in most of this work. The yield was as high as that which has been obtained with amyl chloride and benzene (78%)[4] but the resulting phenylsodium was less reactive with toluene so that the quantities of phenylacetic and phenylmalonic acids were below those produced by the former method. This result is probably due to the higher temperature (85 instead of 55°) necessary for exchange. Indeed, when the time at 85° was extended or the temperature raised to 110° the yield dropped appreciably. Indicative also of lower activity of this phenylsodium was the failure of methyl iodide to give ethylbenzene unless the exchange mixture were heated to 85° though this reagent uncovered evidence of metallation at room temperature in the case of the reactive phenylsodium from amyl chloride, benzene, and sodium.[2] The physical appearance of the two phenylsodiums was also different, that from chlorobenzene being a black powder which settled quickly when stirring was stopped so that an almost clear solution resulted. The green phenylsodium from amyl chloride, on the other hand, remained suspended for some time.

Attempts to use benzyl chloride and benzal chloride as sources of mono- and di-sodium compounds, respectively, were unsuccessful, either because the sodium compound formed was too reactive for isolation in the presence of incoming

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(*) Original manuscript received April 17, 1939.

[1] Morton and Fallwell, Jr., THIS JOURNAL, 59, 2387 (1937).

[2] Morton, Fallwell, Jr., and Palmer, *ibid.*, 60, 1426 (1928).

[3] Morton and Fallwell, Jr., *ibid.*, 60, 1429 (1938).

[4] Morton and Hechenbleikner, *ibid.*, 58, 2599 (1936).

benzyl chloride or because little or no reaction occurred with the metal. Behavior of the disodium compounds with other di-halogen compounds such as pentamethylene dibromide and benzal chloride also was tried but no evidence of the expected reaction was found.

Experimental

Heptene-2.—Amylidenedisodium was made in the usual manner[1] from 63.9 g. (0.6 mole) of amyl chloride and 37 g. (1.6 atoms) of sodium at 20–25° in a special cut of petroleum ether which boiled below 45°. It reacted vigorously when 23 g. (0.24 mole) of ethylidene chloride was added. Fractionation of the product yielded 2 g. of material boiling at 50–95° and 3.8 g. at 95–97°. The latter was strongly unsaturated when tested with bromine water and corresponded in boiling point with that recorded[5] for heptene-2 (97.8°); boiling point of dibromide 95–96° at 12 mm.; refractive index 1.4997. Recorded values were 96.2° at 12 mm. and 1.5000, respectively. The yield was 13% calculated on an amyl chloride basis. A higher boiling fraction, 110–115° at 120 mm. amounting to 5.2 g., was examined in hope that it might prove to be 6-ethylundecane but was found to have a molecular weight (Rast) of 226, and to be unsaturated to bromine.

Under similar conditions methylene chloride was added to amylidenedisodium which had been prepared in solvent ligroin carefully fractionated to remove material boiling below 85°. After decomposing in the usual manner a fraction unsaturated to bromine and boiling 61–66° corresponding to hexene-1 was obtained.

Phenylsodium from Chlorobenzene and Its Exchange with Toluene.—Chlorobenzene, 68 g. (0.6 mole), was added with stirring to 37 g. (1.6 atoms) of fine sodium sand which had been activated by addition of 5 ml. of *n*-amyl alcohol while suspended in petroleum ether. Reaction was very sluggish below 30° whereas amyl chloride reacts smoothly below 0°. After two and one-half hours required for addition of chlorobenzene, the mixture was stirred one hour longer before adding 135 g. of toluene and refluxing at 52° for two hours. Carbonation showed that this phenylsodium was relatively inactive, no exchange having occurred. The yield of benzoic acid was 53.5 g. (79%). Diphenyl, 2.7 g. (8%), also was recovered. Addition of methyl iodide in place of carbon dioxide likewise failed to show occurrence of any exchange, 35 ml. or 55% excess toluene being recovered.

When the above experiment was repeated, enough petroleum ether was distilled from the reaction mixture after addition of toluene to make the boiling temperature 85°. The mixture was maintained with stirring at this temperature for two hours before carbonation: yield of phenylacetic acid 21.6 g. (26%); of phenylmalonic acid 19.1 g. (35%). A similar experiment in which more petroleum ether was distilled from the mixture so that the exchange temperature with toluene was 106° produced 14.2 g. (17%) of phenylacetic and 21.2 g. (39%) of phenylmalonic acid. Separation of acids from this and a number of other experiments in which the exchange temperature was 106 to 115° was complicated by presence of an oily impurity which was removed only after repeated precipitations and extractions. In all cases yields were progressively lower with increasing temperatures of metallation.

Exchange of phenylsodium with toluene gave low yields when the organosodium compound was heated for some time before adding all of the toluene. Thus, phenylsodium prepared from 0.6 mole of chlorobenzene in 250 ml. of benzene was treated successively with 30-g. and 200-g. portions of toluene, each addition being followed by heating at 85° for one and one-half hours. Exchange was not complete, for on carbonation 2.6 g. (3.6%) of benzoic acid was found with 13.1 g. (16%) of phenylacetic acid and 13.8 g. (26%) of phenylmalonic acid. Addition of 215 ml. of toluene to a similar preparation of phenylsodium followed by heating at 85° for two hours yielded 2.2 g. (3%) of benzoic acid, 12.4 g. (22%) of phenylacetic acid, and 16.9 g. (31%) of phenylmalonic acid. It was necessary, however, to heat for some time to effect an exchange at 85°, for holding the temperature at 85° for five minutes (the experiment was identical in other respects with the one using petroleum ether as a solvent) yielded benzoic acid, 28 g. (38%), phenylacetic acid, 2.5 g. (3%) and phenylmalonic acid, 11.4 g. (20%).

Styrene.—Preparation of organosodium intermediates from toluene and phenylsodium was made at 85° as first described. A vigorous reaction ensued as methylene chloride, 16.9 g. (0.2 mole), was added as quickly as possible over a thirty- to forty-minute interval, the reaction temperature being kept at 35° while the kerosene bath temperature was maintained at −10° by addition of dry-ice. The mixture was stirred at 30° for one-half hour longer and then carbonated to ensure that all possible products had been obtained. After decomposing excess sodium by adding water (care must be taken that the first few portions of water have had time to react before more is added) directly to the reaction flask under an atmosphere of carbon dioxide, the organic layer was separated, washed twice with water, once with dilute acid, and three times again with water before distilling through a fifteen-plate column. By careful fractionation at a 15 to 1 reflux ratio over a period of two and one-half days, a fraction beginning at 78° and 160 mm., containing some amyl alcohol, and ending at 104° and 6 mm. (when diphenyl began to crystallize in the condenser), was obtained which gave, upon reaction with bromine in carbon tetrachlorde, 2.7 g. (3.3%) of styrene dibromide, m. p. 69–71°. The pure material is reported[6] melting at 73°.

Anal. Calcd.: Br, 60.6. Found: Br, 60.3. No acids were recovered by acidifying the water layer.

In an experiment with a larger quantity, 112.5 g. (1 mole) of chlorobenzene and 61 g. (2.6 atoms) of sodium sand there was obtained 5 ml. of the fraction which contained styrene at 90–92° and 27 mm., 6.4 g. (8%) of diphenyl at 129–132° at 11 mm., and 19 ml. of a fraction boiling 145–149° at 8 mm. corresponding to diphenylpropane.

To discover some of the factors affecting the yield of styrene, *i. e.*, of benzylidenedisodium, a series of runs was made. For each set of conditions, reactions with carbon dioxide, methyl iodide, and methylene chloride were successively tried. Results are listed in Table I with the theoretical amount of benzylidenedisodium possible cal-

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[5] Soday and Boord, THIS JOURNAL, **55**, 3293 (1933).

[6] Von Miller, *Ber.*, **11**, 1450 (1878).

culated as the difference between total acids and ethylbenzene. Where toluene was formed from unreacted phenylsodium and methyl iodide the amount was added to that of ethylbenzene in estimating the quantity of styrene possible. No diphenylethane was found among products of the reaction with methyl iodide.

TABLE I

ESTIMATION OF MONO- AND DI-SODIUM INTERMEDIATES PRESENT FROM REACTION OF PHENYLSODIUM WITH TOLUENE UNDER VARYING CONDITIONS

Products	Percentage yields obtained for condition *a*	*b*	*c*
Benzoic acid		19	24
Phenylacetic acid	26	14	7
Phenylmalonic acid	35	18	23
Total acids	61	51	54
Ethylbenzene	46	35	22
Toluene	..	13	15
Total monosodium, acid	46	48	37
Styrene Theoretical	15	3	17
Styrene Observed	3.3	1.4	2

[a] Phenylsodium prepared from chlorobenzene in petroleum ether and exchange carried out at 85° as described earlier in this paper. [b] Phenylsodium prepared from 0.6 mole of chlorobenzene in 250 ml. of benzene followed by addition of 30 g. of toluene and heating for two hours at 84°. [c] Same as in (*b*) except that 15 g. of toluene was added, the mixture heated for one and one-half hours at 82°, 15 g. additional toluene then added, and the mixture again heated for two hours at 83°. The purpose of conditions (*b*) and (*c*) was to test if a deficiency of toluene favored formation of benzylidenedisodium; the result actually revealed that phenylsodium had been inactivated by heat.

Methylstyrene.—Benzylidenedisodium was prepared from phenylsodium (chlorobenzene source) at 85° and treated with 23 g. of ethylidene chloride added gradually at 35° over a period of one hour. The product was then carbonated and decomposed with water. Acidifying the water layer gave no acids recoverable by ether extraction. On careful fractionation of the hydrocarbon layer a portion boiling from 85 to 95° at 70 mm. and amounting to 12 g. was found to be unsaturated to bromine water. The dibromide isolated amounted to 2.7 g. (3%), m. p. 63–64°; recorded[7] value 66.5°. Analysis for bromine in this sample showed a value high enough (56.7%, theory 57.5) to distinguish it from any other possible product.

Benzylsodium and Dimethyl Sulfate.—The organosodium intermediates were prepared from 112.5 g. (1 mole) of chlorobenzene and other reactants in proportion. After heating for two hours at 85° in order to metallate toluene, the mixture was cooled to 35° and treated with 70 g. (0.55 mole) of undiluted dimethyl sulfate over a two and a half hour period. Addition was discontinued as soon as heat ceased to be evolved. After decomposition the hydrocarbon layer was washed with sodium carbonate several times and then twice with water but on distillation some decomposition with evolution of sulfur dioxide began. Distillation was therefore halted until the mixture had been steam distilled. The distillate was then fractionated under a 10 to 1 reflux ratio through the fifteen-plate column whereupon 46 g. (43%) of ethylbenzene, b. p. 134–134.8°, was obtained. No fraction corresponding to isopropylbenzene was found. Above 200° sulfur dioxide fumes were evolved.

Reaction with Phenylethyl Chloride.—Benzylidenedisodium, with the accompanying benzylsodium, was made in the same manner employed for the styrene experiment except that 30.3 g. of chlorobenzene with a proportionately smaller amount of sodium was used. β-Phenylethyl chloride, 25 g. (0.18 mole), Eastman Kodak Co. grade, was added in place of methylene chloride. After decomposing and fractionating no dibromide could be isolated nor could even a test for unsaturation be detected in the fraction which should have contained styrene. Diphenylpropane was the only product obtained from this experiment.

Reaction with Benzal Chloride.—The mixture of benzyl sodium and benzylidenedisodium was treated dropwise with 29 g. (0.18 mole) of benzal chloride which had been distilled just before use. Fractionation of the hydrocarbon layer obtained after decomposing excess sodium gave at 6 mm. and a reflux ratio of 10 to 1: at 104–106°, 4.1 g. of diphenyl; at 106–129°, 1 g. of a liquid; and at 129–132°, 6.2 g. of a liquid which crystallized upon chilling and scratching, m. p. 46–48°. Several crystallizations from petroleum ether did not raise its melting point above 51–51.5°. No depression was observed with an authentic sample of diphenylethane.

Reactions of Benzyl and Benzal Chlorides with Sodium.—Benzyl chloride, 76 g. (0.6 mole), was added at 25° to 37 g. (1.6 atoms) of sodium sand which had been activated by addition of 5 ml. of amyl alcohol. Petroleum ether, 300 ml., was used as the solvent. There was an immediate reaction and the mixture became blue-black in color. No heat was evolved on carbonation and the product after decomposing in the usual manner had a strong odor of unreacted benzyl chloride. After distilling up to 200° at atmospheric pressure, the residue crystallized, giving 29.1 g. of diphenylethane. The yield was 51%, no allowance being made for unreacted benzyl chloride. The reaction was repeated using petroleum ether, 300 ml., and toluene, 50 ml., as the solvent in the hope that benzylsodium would be stable in this mixed solvent as it had once before[4] proved to be when amyl chloride had been used. Again no acids were found after carbonation. Some unreacted benzyl chloride was present, and the yield of dibenzyl was 20 g. (45%).

Benzal chloride, 48.3 g., was added to 37 g. of sodium sand in the same manner first tried with benzyl chloride above. No acids were found after carbonation. A considerable quantity of unreacted benzal chloride was present but the products in general were difficult to separate. A small amount of stilbene, m. p. 118–120°, was isolated.

Pentamethylene Dibromide with Benzylidene- and Amylidenedisodium.—Benzene, 300 ml., was added to phenylsodium from 0.6 mole of chlorobenzene and 1.6 atoms of sodium in 250 ml. of petroleum ether. After distilling until the temperature of the mixture reached 78°, 60 ml. of toluene was added, the mixture refluxed at 86° for two hours, cooled to 25°, and treated dropwise with 36 g. (0.16 mole) of pentamethylene bromide[8] over a one

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[7] Rügheimer, *Ann.*, **172**, 131 (1874).

[8] Von Braun, "Org. Syntheses," Coll. Vol. I, 1932, p. 419.

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 amylidenedisodium, 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's[10] procedure for making the diacetamino derivative.

Summary

Ethylidene chloride reacts with amylidenedisodium 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 amylsodium.

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.

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[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 amylidenedisodium) 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 amylidenedisodium (butylmalonic acid) was attributed[1] 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

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