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 Peakes[5] 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.

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

[Contribution from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology, No. 208]

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-Bergmann[2] 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

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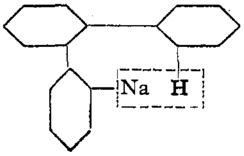
[1] Bachmann and Clarke, This Journal, **49**, 2089 (1927).

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

could be metallated in the ortho position giving *o*-phenylbiphenylsodium, which then would split out sodium hydride after the general method suggested for ethylsodium by Carothers[3] to form triphenylene. Under the conditions for isolating intermediate organometallic compounds employed in our work, triphenylene was shown to occur to a small extent from the reaction of chlorobenzene with sodium. Yet no evidence of metallation of *o*-phenylbiphenyl or of biphenyl itself by phenylsodium could be obtained. It is true that both of these hydrocarbons were metallated by amylsodium but no indication was observed that sodium hydride split from such a substance and formed triphenylene. Neither did the carrying out of a reaction between chlorobenzene and sodium in the presence of *o*-phenylbiphenyl produce any measurable conversion of that material into triphenylene.



The second proposition is that chlorobenzene could be metallated by phenylsodium giving chlorophenylsodium which could then condense with two similar molecules to give triphenylene. Substance is given to this idea by the work of Goldschmidt and Schön[4] suggesting that sodium and iodine might be present together in the cresol molecule, and by the work of Wittig[5] and of Gilman[6] in which lithium and bromine were likewise substituents together in methoxy containing compounds such as dimethoxybenzene and anisole. In the latter work indeed reference was made to a private communication from Wright that chlorobenzoic acid was obtained by carbonating the product of the reaction of chlorobenzene with sodium. Under conditions employed in our work, however, there is no evidence that a similar reaction occurred here. We have tested the action of both phenyl- and amylsodium on chlorobenzene under conditions which favor isolating such an intermediate product and find after carbonating no trace of chlorobenzoic acid.

Although the free radical mechanism is a convenient vehicle for expressing the manner in which triphenylene is formed, it does not necessarily follow that a similar mechanism has been demonstrated for occurrence of biphenyl, for the presence of such a small amount of triphenylene is equally explicable on the basis of its being the result of a side reaction wholly unrelated to the main one. In this connection it is worth noting that the free radical, phenyl, obtained by decomposition of phenylazotriphenylmethane by Wieland[7] showed no tendency to form biphenyl. The general comments relative to radicals (free or in a complex) and the role of organometallic compounds in Wurtz syntheses as mentioned in the paper just previous are worthy of consideration in this case also.

Experiments

Triphenylene and other Phenylated Polymers. (J. T. M.).—Formation of triphenylene under conditions employed in our work for isolating intermediate organometallic compounds was demonstrated by combining the high-boiling residues from nine separate experiments, in which chlorobenzene[8] (total of 550 g., 5.8 moles) had been added to sodium at room temperature to obtain a yield of approximately 75% of phenylsodium which was later used to metallate toluene. These high-boiling ends were distilled carefully through a fifteen-plate column. Out of 14.1 g. collected in three fractions from 135 to 155° at 2 mm., a total of 4.6 g. *o*-phenylbiphenyl, m. p. 52–53° (recorded[1] value 57°) was collected. A mixed melting point with an authentic sample (m. p. 55°) gave a value of 53–54°. The uncrystallizable oil from this fraction was adsorbed from a petroleum ether solution on 40–60 mesh activated alumina, giving several short indistinct bands at the top of the tube and one long band with deep blue fluorescence under the ultraviolet light. This last band was extracted with benzene yielding 0.9 g. of additional *o*-phenylbiphenyl, making a total of 1.5%.

From the fraction boiling from 155 to 165° there was isolated 0.3 g. of material melting at 144 to 146° which was not identified. The residue from the above distillation was distilled in a molecular still and the 4.8 g. of distillate was chromatographically adsorbed as described above. Several indistinct bands of a yellowish tint were in the top of the tube and one long band with a very bright blue fluorescence under the ultraviolet light in the lower portion. This material was also removed by benzene from which on evaporation fine needle-like crystals separated out of a viscous mother liquid. These were identified by their melting point of 192–194° (recorded[1] 199°, cor.) and by a mixed melting point (193–195°) with an authentic sample. The residual yellow liquid was dissolved in a mixture of petroleum ether and benzene and allowed to evaporate over a period of several days whereupon a mass of fine needle-like crystals and ten large diamond-shaped

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

(4) Goldschmidt and Schön, *Ber.*, **59**, 948 (1926).

(5) Wittig, Pockels and Dröge, *Ber.*, **71**, 1903 (1938).

(6) Gilman, Langham and Jacoby, THIS JOURNAL, **61**, 106 (1939).

(7) Wieland, Popper and Seefried, *Ber.*, **55**, 1816 (1922); Wieland. *Rec. trav. chim.*, **41**, 576 (1922); see also Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

(8) Morton and Massengale, THIS JOURNAL, **62**, 123 (1940).

crystals were deposited. The residual oil was sucked off by vacuum filtration and the crystals were washed quickly with a mixture of benzene and petroleum ether. The ten large crystals were then picked out with a pair of tweezers and brushed clean from the needles. Their weight was 0.1 g., melting point 115–117° (recorded[1] value for *o,o'*-diphenylbiphenyl is 118°) and mixed melting point with an authentic sample 117°.

Metallation of *o*-Phenylbiphenyl. (J. T. M.).—Phenylsodium was prepared from 64 g. (0.6 mole) of amyl chloride, 37 g. (2.7 atom equivalents) of sodium sand activated by 5 ml. of *n*-amyl alcohol in 600 ml. of benzene. Phenylbiphenyl, 10 g., was added and the solution stirred and refluxed at 73° for nineteen hours before cooling and carbonating. On distillation 81% of the phenylbiphenyl was recovered intact, together with smaller amounts contaminated with adjacent fractions. No trace of triphenylene could be detected in the final residue. The acid recovered proved to be entirely benzoic and amounted to 33 g. (46%).

The experiment was repeated and methyl iodide, 60 g. (0.42 mole) instead of carbon dioxide added to the supposedly metallated *o*-phenylbiphenyl since methyl iodide once before[9] proved to be a more sensitive reagent for testing occurrence of an exchange reaction. Toluene was the chief product and 91% of the 7.5 g. of *o*-phenylbiphenyl originally added was recovered pure. The remainder was present as contamination in adjacent fractions. No trace of triphenylene could be noted.

Amylsodium was prepared from 8 g. of amyl chloride and 2.7 equivalent atoms of sodium sand in 100 ml. of petroleum ether. *o*-Phenylbiphenyl, 11.3 g., was added, the mixture warmed for thirty minutes at 40° and then carbonated. A mixture of acids with a neutralization equivalent of 189 between that for a mono- (284) and a dicarboxylic acid (164) of the phenylbiphenyl compound was obtained after separating the benzoic acid. The unchanged hydrocarbon amounted to 80% and no trace of triphenylene was noted.

Phenylsodium was prepared from 30 g. of chlorobenzene and 6 g. of sodium sand in the presence of 7.5 g. of *o*-phenylbiphenyl in order to see whether the reaction in the presence of this hydrocarbon would provoke ring closure or if the hydrocarbon would be metallated. After four hours of stirring at 40° and carbonating the products, 30% of benzoic acid and 20% of diphenyl was obtained. Of the original hydrocarbon, 90% was recovered unchanged in one fraction. No triphenylene corresponding to the missing 10% could be noted.

Metallation of Diphenyl. (G. M. R.).—When amylsodium from 150 ml. of amyl chloride and 75 g. of sodium in petroleum ether were stirred for eighty-eight hours with 12 g. of biphenyl at room temperature, the mixture after carbonation showed definite evidence of the expected metallation. Caproic acid, 4.7 g. (3%) and ether soluble acids (13%) were recovered. From the brown gummy residue, after ether evaporation, a white crystalline acid, 0.7 g., with neutralization equivalent of 188 and melting point of 205° in the crude state was obtained. It appeared to be *p*-phenylbenzoic acid (224°). On purifying and converting to the methyl ester a melting point of 116–117° (recorded[10] value 117–118°) was obtained. More of this same material (0.7 g.) precipitated from a petroleum ether wash of the residue and 0.4 g. of still more impure material of similar properties was obtained on further extraction with petroleum ether. The residue consisting of 1.9 g. was extracted with ether, acetic acid and benzene and appeared to be a mixture of di- and tri-substituted acids but no definite product was isolated. The non-acid portion contained no biphenyl but after evaporation left 2.7 g. of a thick amber colored liquid which was distilled in a molecular still at temperatures ranging from 114 to 230°. From the three fractions thus collected no crystalline derivative such as might be expected from splitting out of sodium hydride from two molecules could be obtained.

Metallation of biphenyl by phenylsodium failed when a mixture of 8.8 g. of biphenyl in 100 ml. of benzene was added to amylsodium prepared from 38 g. of amyl chloride and 35 g. of sodium (activated by 2.5 ml. of amyl alcohol) in benzene at room temperature. After stirring at 27° for two hours and at 75° for one and one-half hours, the mixture was carbonated. No trace of acids of biphenyl could be noted, although 9.7 g. (26%) of benzoic acid was obtained. Curiously enough, 5.5 g. (22% or the usual amount) of butylmalonic acid was found, presence of biphenyl apparently being sufficient to prevent the exchange of amylidenedisodium with benzene even at 75°.

Attempted Metallation of Chlorobenzene. (J. T. M.).—The Beilstein[11] test was found to be unreliable as a test for halogen in benzoic acid since the purest samples could be made to give a green color. In order to test for very small traces of chlorobenzoic acid, 30 g. of pure benzoic acid and 0.1 g. of chlorobenzoic acid were treated with ethyl alcohol, benzene, and sulfuric acid as a catalyst, the water removed to effect complete esterification by means of a ternary mixture under a fractionating column of fifteen plates, the mineral acid separated by washing, and the ester then distilled. Chlorine could be detected readily in the last 1 ml. of distillate, either by the Beilstein test or by sodium fusion and subsequent testing with silver nitrate. In parallel experiments with benzoic acid, no chlorine could be observed. This method was applied to the combined benzoic acid residues from a number of preparations of phenylsodium from chlorobenzene and sodium but no evidence of chlorobenzoic acid could be found. Furthermore, a mixture of 11 g. of amyl chloride and 12 g. of chlorobenzene (0.1 mole of each) was dropped onto 0.5 atom of sodium in 200 ml. of petroleum ether. Addition and stirring time were one-half hour each. The temperature during these periods and during carbonation did not exceed 3° in order to make the conditions as favorable as possible for isolating chlorophenylsodium. The yield of benzoic acid was 1.9% based on the combined reactants and contained no detectable trace of chlorobenzoic acid when tested in the above manner. The hydrocarbon layers likewise gave no halogen tests in the fraction which boiled above the boiling point of chlorobenzene.

Phenylsodium was prepared from 43 g. of amyl chloride and 24 g. of sodium in benzene in the usual manner and treated dropwise with 68 g. of chlorobenzene over a period

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[9] Morton and Fallwell, This Journal, **60**, 1426 (1938).

[10] Meyer and Hofmann, *Monatsh.*, **38**, 353 (1917).

[11] Similarly the Beilstein test for chlorine was found (G. M. R.) to be worthless in the case of caproic acid.

of one hour and a half before carbonation. The mixture of acids obtained from this experiment gave no halogen test. Similarly amylsodium was prepared in petroleum ether and the mixture stirred for four hours at room temperature before carbonation. Tests for halogen in the acid and hydrocarbon fractions were negative.

Summary

o-Phenylbiphenyl and biphenyl are not metallated by phenylsodium but are by amylsodium.

Under the conditions in which organometallic compounds are isolated in this work no evidence of metallation of chlorobenzene could be detected.

Triphenylene is not formed under the conditions of this work either as a result of metallation of *o*-phenylbiphenyl or of chlorobenzene.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 7, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 209]

Condensations by Sodium. XVIII. A Study of the Possible Conversion of Amylsodium to Amylidenedisodium

BY AVERY A. MORTON AND GRAHAM M. RICHARDSON

In an earlier paper[1] primarily connected with formation of phthalic acid, curves related to exchange of amylsodium with benzene showed that with small amounts (5 ml.) of benzene a drop in yield of caproic acid appeared with an increase of butylmalonic acid. These results suggested conversion of amylsodium into amylidenedisodium at 42° and necessitated reëxamination of the subject. As a result of an extensive investigation we find: (a) that higher yields of butylmalonic acid are more apt to be obtained if the mixture of organosodium compounds is heated at 42° or stirred for a long time at room temperature but the results are very erratic and if such a change occurs it does not exceed 10%; (b) that at −15° where the experiments proved quite reproducible no hint of such a change has been observed even on long stirring; (c) that when benzene is used as a trap at room temperature amylidenedisodium is still formed. These results, together with the earlier work on this subject, confirm the original opinion[2] that the chief source of amylidenedisodium is not by way of amylsodium. Subject to the restriction on the nature of free radicals in these solutions as discussed in two papers just previous in this series, the view of a radical origin for this material appears the most reasonable.

Irrespective of whether conversion actually occurs, warming at 42° is reasonably successful as a general method of increasing the yield of butylmalonic acid. Higher temperatures (70–80°) have earlier[3] been shown to lead to decomposition. The erratic results (see Tables I and II) at 42° are probably due to thickening of the reaction mixture when warmed, a difficulty absent at −15°.

In hope that a nickel catalyst would labilize the hydrogen atom and promote the hoped for change, experiments were made in the presence of this metal. The results were unexpected in that no increase in butylmalonic acid was observed and that portion of the amylsodium which formerly had been converted to the disodium intermediate, was decomposed. Apparently a small amount only of the amylsodium is active, possibly because of particle size or because of a complex salt structure.

It might be argued from these facts that the original amylidenedisodium present before heating at 42° owed its origin also to a certain proportion of very active amylsodium. Against this notion some experiments in benzene can be cited. Amylsodium reacts readily with benzene at room temperature, thereby making it possible to use it as a trap. Amylidenedisodium reacts more slowly so that it is possible to find butylmalonic acid among the products of carbonation when addition of amyl chloride to sodium is made in benzene at room temperature. Indeed, when biphenyl was present (preceding paper) the disodium compound apparently was protected and the quantity of butylmalonic acid was essentially the same as when petroleum ether was the solvent. An especially active amylsodium, however, would be expected to be more active also toward benzene so that little or no disproportionation should occur. The same argument applies also to the

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

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

[3] Morton and Hechenbleikner, *ibid.*, **58**, 1697 (1936).