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.

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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).

experiments under pressure of carbon dioxide reported[4] early in this series.

In the curve referred to at the beginning of this paper a second minimum (total acids) in addition to the first already discussed, was noted when a larger amount of benzene was added. This second point is now shown to be due in all probability to physical factors such as stirring. The reaction mixture becomes very thick during this exchange reaction and erratic results are therefore possible. As a result of a considerable number of experiments under greatly improved stirring, we find that it is possible to eliminate this second minimum entirely. Erratic results are still secured but under proper agitation the number is reduced materially. The reconstructed curve (Fig. 1) suggests that amyl- may be more closely related to phenyl-sodium and amylidenedisodium to phenylenedisodium than was at first suspected.

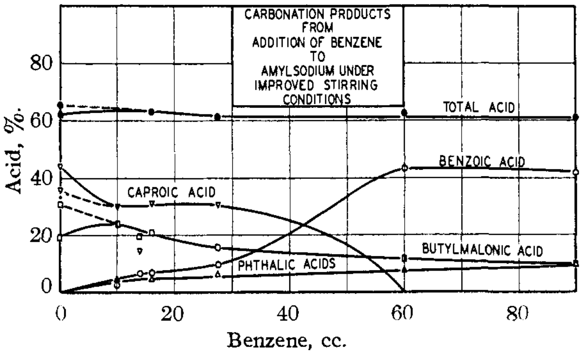

Fig. 1.—Carbonation products from addition of benzene to amylsodium under improved stirring conditions.

Much effort has been spent in order to effect 100% metallation of benzene by excess amylsodium in hope that the procedure would be useful in identification or analysis of benzene in certain petroleum fractions. The best results, however, did not reveal more than 50% of benzene converted to phenylsodium. In contrast to these results biphenyl is completely removed by amylsodium as shown in the paper just previous. This greater susceptibility toward metallation by amylsodium of biphenyl over benzene is particularly interesting since phenyl appears to have a greater affinity for sodium than the biphenyl radical.

Experiments

Effect of Warming Amylsodium.—The general conditions described in the two previous papers were applied to this work. Amyl chloride[5] was distilled before use and a fraction boiling at 107–108° was used. The quantities employed and the results obtained are listed in Tables I and II.

TABLE I

AMYLSODIUM PREPARED AT 18 TO 22°

Constant factors: amyl chloride 37.5 ml. diluted with 25 ml. of petroleum ether; sodium 17.5 g. activated with 2 ml. of *n*-amyl alcohol; petroleum ether 150 ml. at start of the reaction, more being added as the mixture thickened on heating; addition time one and one-half hours; carbonation at 22 to 28°.

	Hrs. stirring time at		Yields of acids				
			Caproic		Butylmalonic		Total,
No.	27°	42°	G.	%	G.	%	%
1	1	0	15.8	43	4.7	19	62
2	3	0	13.0	36	4.5	18	54
3	4	0	10.9	30	7.4	30	60
4	6	0	13.0	36	4.5	18	54
5	1	2	12.5	35	7.6	31	66
6	1	2	14.5	40	4.5	18	58
7	4	2	14.8	41	5.9	24	65

Attention is called to the first four experiments in which the time of stirring was gradually lengthened. In the four-hour period a yield of 30% of butylmalonic acid with a decreased yield of caproic acid was obtained. The inconsistency of this result is shown in experiment 4, in which such a change could not be effected even in six hours. Experiment 5 likewise gives a high yield of the dicarboxylic acid which was not duplicated in 6. Experiment 7 was intended to be a combination of the two best conditions noted before. Although the yield of the malonic acid in this case was disappointingly low, it nevertheless was the third highest in the whole series.

TABLE II

ADDITION OF AMYL CHLORIDE AT 0 TO −4°

Constant factors: amyl chloride 20 ml. diluted with 40 ml. of petroleum ether; sodium 30 g. activated by 2 ml. of *n*-amyl alcohol; petroleum ether 150 ml. at start of the reaction; addition time one hour; carbonated at 0 to −4°.

	Hrs. stirring time at		Yields of acids				
			Caproic		Butylmalonic		Total
No.	0–4°	42°	G.	%	G.	%	%
8	3.5	0	11.0	58	2.9	22	80
9[a]	0.5	0	10.8	56	2.5	20	76
10	.5	0	11.5	60	3.0	23	83
11	.5	1	11.5	60	3.4	26	86
12	.5	2	13.1	68	3.1	21	89
13	.5	2	10.9	57	2.4	18	75
14	.5	3	10.1	53	4.0	31	84
15	.5	8	9.8	51	3.6	27	78

[a] Special attention is called to the changes which occur in experiments 9 to 15, in which the time of heating at 42° gradually was extended to eight hours.

In one experiment only could the yield of butylmalonic acid be raised to 31% although the second highest yield was one in which long heating had been applied. The only suggestion of consistency in these results is that the two experiments which were heated for the longest time

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[4] Morton and Hechenbleikner, THIS JOURNAL, **58**, 754 (1936).

[5] Amyl chloride was furnished by the courtesy of the Sharples Solvent Corporation.

had the highest yields of butylmalonic acid and the lowest yields of caproic acid.

In another experiment, using the same quantity of reagents given in Table II but carrying out the addition at −15 to −20°, the stirring time at that same temperature was varied from one-half hour to four hours. Carbonation at the same low temperature resulted in the same yields in both cases for butylmalonic acid, 2.9 g. or 22% but the yield of caproic acid fell during that period from 13 to 11 g. (68 to 59%).

Experiments with a Nickel Catalyst.—The conditions were the same as those employed in Table II except that nickel catalyst prepared from 4 g. of Raney nickel was employed under the conditions specified.

TABLE III

No.	Hrs. stirring time at 0 to −4°	42°	Yields of acids Caproic G.	%	Butylmalonic G.	%	Total %
16	3.5[a]	0	11.5	60	3.0	23	83
17	0.5[a]	3	10.1	53	2.4	18	71
18	.5[b]	3	10.0	52	3.0	23	75

[a] Catalyst present during addition of amyl chloride. [b] Catalyst added after addition of amyl chloride.

Experiment 16 was almost an exact duplicate of experiment 8 in Table II and shows that nickel was without appreciable effect as long as the mixture was not heated. Experiment 17 is a duplicate of number 14 and shows that while caproic acid decreased the butylmalonic acid was not increased. Experiment 18 likewise shows the effect of nickel on amylsodium. Yields of caproic acid in 17 and 18 are as low as the two lowest in Table II.

Experiments in Benzene.—The results listed in Table IV show the formation of amylidenedisodium (butylmalonic acid) from amyl chloride and sodium in presence of solvent used as a trap for amylsodium. Addition temperature in all cases was at 18–22°. Carbonation temperature was at 22 to 28°. All results and special conditions are listed in the accompanying table with explanatory notes.

TABLE IV

No.	Yields of acids Benzoic G.	%	Butylmalonic G.	%	Total %
19[a]	14.4	38	2.5	10	48
20[b]	30.0	40	3.3	7	47
21	27.9	37	4.9	10	47
22	9.7	26	5.5	22	48

[a] Experiment 19: amyl chloride 37.5 ml., sodium 53 g. activated by 7.5 ml. of amyl alcohol, 500 ml. creased flask as a reaction vessel. Addition time three hours, stirring at 27° for one hour. [b] Experiment 20: amyl chloride 75 ml., sodium 35 g., 1-l. three-necked flask as a reaction vessel, addition time two and one-half hours. Stirring time four hours at 27°. From among the products phthalic acid (iso- and tere- mixture) 3.2 g. or 6% was isolated also. In experiment 21, conditions were the same as in 20 except that a 1-l. creased flask was used as the reaction vessel. Experiment 22 is the one which contained biphenyl and is described in the paper immediately preceding. A trace of the phthalic acid was formed.

Exchange Reaction of Amylsodium with Benzene.—In these experiments a 500-ml. creased flask was used to effect better agitation. Amyl chloride, 37.5 ml., mixed with an equal quantity of petroleum ether was added dropwise over a one and one-half hour period to 35 g. of sodium sand activated with 5 ml. of alcohol, and suspended in 250 ml. of petroleum ether; addition temperature was 18 to 22°. After addition was complete the mixture was stirred at 25 to 30° for one hour. Benzene was then usually added and the mixture with or without benzene heated at 42° for two hours. Carbonation was at 22 to 28°. Quantities of benzene added in separate experiments were 10, 14, 16, 27.5, 60 and 90 ml. Corresponding yields of acids are caproic: 10.7, 5.4, 11.2, 11.0, 0 and 0.9 (30, 15, 31, 0, 0.7%); butylmalonic acid 5.9, 4.9, 5.1, 3.9, 2.9 and 2.5 g. (24, 20, 21, 16, 12 and 10%); benzoic acid, 1.1, 2.5, 2.5, 3.5, 16.4 and 15.8 g. (3, 7, 7, 9, 43 and 41%); phthalic acid 1.1, 0.7, 1.2, 1.6, 2.0 and 2.5 g. (4, 3, 5, 6, 8 and 10%). In the graph the values for zero benzene are from two separate observations in one of which (dotted line) the conversion did not occur.

Attempted Quantitative Metallation of Benzene.—In addition to the foregoing experiments, 5 ml. of benzene was put in the solvent before addition of amyl chloride and treated in the usual manner. Not more than 28% of this benzene was converted to benzoic and phthalic acids. In another case, 5 ml. of benzene was added after addition of amyl chloride was completed and the mixture then stirred at room temperature for seventy-two hours. In this way 50% of the benzene was converted to acids.

Summary

Amylidenedisodium frequently is obtained in somewhat higher yields if the mixture is warmed at 42° or is stirred for a very long time. Simultaneously lower yields of caproic acid are usually found. These results suggest that amylsodium is capable of being converted into amylidenedisodium but the change is an uncertain one and does not exceed 10% at the most.

Active nickel appears to decompose a portion of the amylsodium at 42°.

Under appropriate conditions butylmalonic acid is one of the carbonation products of the reaction of amyl chloride on sodium in benzene solution although amylsodium is completely removed by the solvent at room temperature.

Small quantities of benzene are not quantitatively metallated by amylsodium.

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