



1942

## A Study of the Preparation of Phenyl Sodium

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A STUDY OF THE PREPARATION OF PHENYL SODIUM

By

William W. Jenkins

A Thesis Submitted in Partial Fulfillment of  
the Requirements for the Degree of Master  
of Science in Loyola University

June

1942

## Vita

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## TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION . . . . .	1
II. PREVIOUS WORK . . . . .	2
Diphenyl mercury method - Metalation - Halobenzene methods - Evaluation of methods.	
III. RESEARCH . . . . .	6
Initial procedure - Apparatus - Fluorene method - Temperature variations - Time variations - Variation of ehmicals.	
IV. DISCUSSION AND CONCLUSION . . . . .	17
BIBLIOGRAPHY . . . . .	20
APPENDIX . . . . .	21

LIST OF TABLES

TABLE	PAGE
I. BROMOBENZENE RUNS . . . . .	14
II. CHLOROBENZENE RUNS . . . . .	16
III. TIME TEMPERATURE RELATIONSHIP .	17

# CHAPTER I

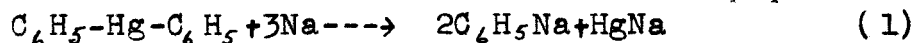
## INTRODUCTION

Phenyl sodium is an organometallic chemical, which classification identifies it as partly organic and partly inorganic. Organometallic compounds are organized into groups according to the metals which they contain. These groups are identical with those of the Periodic Table. Phenyl sodium is in group Ia along with organo derivatives of Potassium, Lithium, Rubidium, Cesium, and element number eighty-seven (Francium).

Since the inception of the Grignard reagent in 1900 the importance of organometallic chemistry has become quite profound, especially in synthetic procedures in organic chemistry. In such procedures the role of the organometallic compound is that of an intermediate. As a result it is highly desirable to standardize and simplify the preparation of organometallic compounds. Of the many such compounds containing sodium, phenyl sodium has shown promising signs of being useful. Therefore a study of phenyl sodium has been undertaken with the purpose of standardizing and simplifying its preparation.

CHAPTER II  
PREVIOUS WORK

The first recorded preparation of phenyl sodium was accomplished by Acree.<sup>1</sup> He employed the metal exchange reaction involving diphenyl mercury and sodium metal according to equation number (1).



The reaction was carried out under an atmosphere of hydrogen. The determination of the amount of phenyl sodium present was accomplished by gaseous carbonation (this reaction is assumed to be quantitative) and subsequent acidification to give an amount of benzoic acid equivalent to 87% phenyl sodium. The reaction was run in benzene and petroleum ether, and a direct analysis under hydrogen of the light-brown suspended matter indicated mostly phenyl sodium and some unreacted diphenyl mercury.

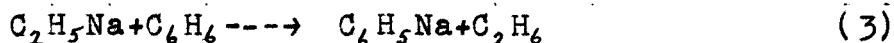
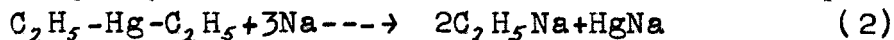
It is interesting to note that Hilpert and Grüttner were unable to reproduce phenyl sodium in the manner above, obtaining only "insoluble, infusible dark products."<sup>2</sup> Schlenk, however, was success-

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<sup>1</sup>S.F.Acree, Am. Chem. Journal, 29, 589 (1903).

<sup>2</sup>S.Hilpert and G.Grüttner, Ber., 46, 1679 (1913).

ful using Acree's method, finding it expedient to remove the phenyl sodium by centrifugal force.<sup>3</sup> Schlubach has also substantiated this work.<sup>4</sup>

An interesting preparation of phenyl sodium was accomplished by Schorigen in 1908.<sup>5</sup> Advantage here was taken of the metal exchange reaction (equation number 2) and the metalation reaction (equation number 3). By the usual method of carbonation (gas-



eous), a yield of 12% of phenyl sodium was reported. Using essentially the same method another source has obtained a 41% yield.<sup>6</sup>

Using diphenyl mercury as a starting material and benzophenone in place of gaseous carbon dioxide a yield of 93%  $\text{C}_6\text{H}_5\text{Na}$  has been reported.<sup>7</sup> Similarly normal amyl sodium has been converted to  $\text{C}_6\text{H}_5\text{Na}$  in 78% yields by the metalation reaction with benzene<sup>8</sup> (reaction is analagous to that given in equation number (3)).

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<sup>3</sup>W.Schlenk and J.Holtz, Ber., 50, 263-4 (1917).

<sup>4</sup>H.Schlubach, Ber., 52, 1914 (1919).

<sup>5</sup>P.Schorigen, Ber., 41, 2725 (1908).

<sup>6</sup>H.Gilman and R.Kirby, J. Am. Chem. Soc., 58, 2074 (1936).

<sup>7</sup>W.E.Bachmann, J. Am. Chem. Soc., 55, 2830 (1933).

<sup>8</sup>A.Morton and I.Hechenbleickner, ibid., 58, 2599-(1936).



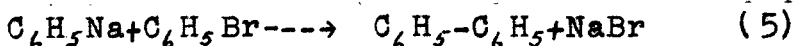
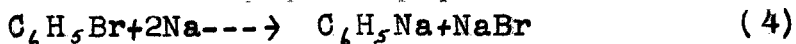
So far we have considered the use of organometallic compounds for the preparation of phenyl sodium. Though the yields in some cases have been excellent, the availability of the starting materials (such as diphenyl mercury and diethyl mercury) constitutes no small problem. For example, diphenyl mercury is obtained from the reaction of phenylmagnesium halide (an organometallic compound prepared from a halo benzene and magnesium) with a mercury halide. From the standpoint of economics the use of such reagents as diphenyl mercury or diethyl mercury is extremely prohibitive. On the other hand, normal amyl sodium (from normal amyl chloride) presents no great economic problem, but its chemical property of being spontaneously flammable in air presents an unfortunate hazard.

Another possible route toward obtaining phenyl sodium was first indicated by Kekule.<sup>9</sup> By heating sodium with bromobenzene on a water bath in the presence of carbon dioxide he obtained among other products some sodium benzoate, which, he postulated, came from phenyl sodium formed. In 1909 Mohr<sup>10</sup>

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<sup>9</sup>F.Kekule, Ann., 137, 178-81 (1866).

<sup>10</sup>E.Mohr, J. prakt. Chem., 80, 318 (1909).

reacted bromobenzene and sodium for eight hours at 45°-55°, and although he too postulated C<sub>6</sub>H<sub>5</sub>Na he found only sodium bromide and diphenyl which he explained by equations (4) and (5).



Since he used three moles of bromobenzene for each gram atom of sodium, it is evident that the overall reaction was one of coupling of the type found in the Wurtz-Fittig reaction.

Much later Schlubach<sup>11</sup> treated bromobenzene with an excess of sodium in a shaking machine and by treating the reaction mixture with carbon monoxide obtained evidence for the presence of C<sub>6</sub>H<sub>5</sub>Na.

Using chlorobenzene and sodium (activated with amylalcohol) a yield of 79% phenyl sodium has been recorded<sup>12</sup>. However, from metalation experiments with toluene, the low yields of expected products were said to be due to the low reactivity of the phenyl sodium. The term "low reactivity" is rather vague, and the inference that phenyl sodium exists

<sup>11</sup>H.Schlubach and E.Goes, Ber., 55, 2898 (1922).

<sup>12</sup>A.Morton and J.Massengale, J. Am. Chem. Soc., 62, 120 (1940).

in more than one state of reactivity has not been substantiated by other workers in the field.

A most successful attempt to prepare  $C_6H_5Na$  from a halobenzene has been recorded in the patent literature<sup>13</sup>. In this instance chlorobenzene was the starting material and in the presence of an inert organic solvent was treated with sodium metal at a reaction temperature between  $15^{\circ}$ - $40^{\circ}C$ . The reaction was carried out in the absence of moisture and oxygen, and yields of better than 90% are claimed, based upon the products obtained by the gaseous carbonation method. Many of the results of the research in this paper are not in entire agreement with this patent. Furthermore, this patent does not disclose enough information for a laboratory duplication of the process, which was the objective of the work undertaken.

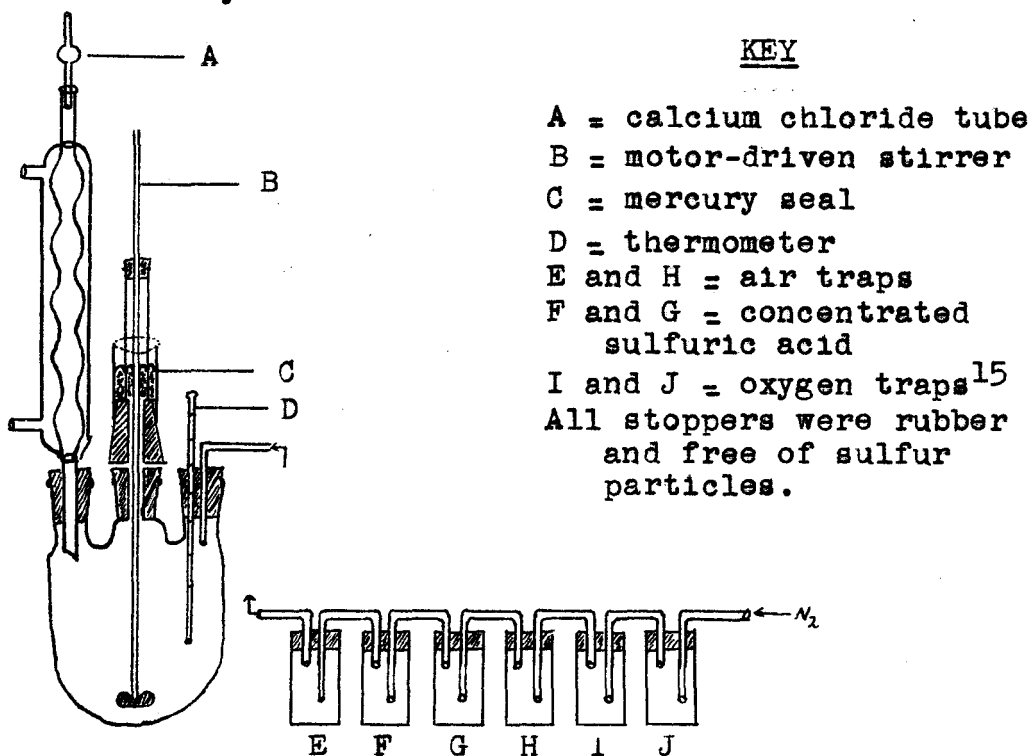
From a standpoint of practicability and simplicity the most logical approach to an accurate and standard preparation of phenyl sodium heavily favors the reaction between a halobenzene and sodium. Research, therefore, was conducted upon this reaction.

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<sup>13</sup>M. Brockmühl and G. Ehrhart, U.S. Patent 2,012,372 (Aug. 27, 1935).

## CHAPTER III

### RESEARCH

Phenyl sodium has been classified as one of the highly reactive types of organometallic compounds,<sup>14</sup> implying that the preparation of phenyl sodium must be conducted in the absence of common substances toward which this compound is reactive (oxygen, water, and carbon dioxide). The apparatus that was used in this study is illustrated below.



<sup>14</sup>H. Gilman, *op. cit.*, p. 440.

<sup>15</sup>In each bottle: 60 grams of pyrogalllic acid, 100 grams pure potassium hydroxide, and 200 c.c. of water.

The procedure given below was used for the initial preparation of phenyl sodium. Alterations in procedure, new terms, etc., which will follow as the complete investigation is given, will be explained as modifications of this initial procedure. Temperatures are all Centigrade.

The apparatus was assembled as shown on page 7 and thoroughly swept out with nitrogen. The sodium was cleanly shaven under petroleum ether (b.p. 80°-110°), weighed, and then powdered in xylene by hand-shaking. The sodium was then freed of xylene by washing three times with petroleum ether and finally washed twice with the solvent which was to be used in the reaction. The mercury-sealed stirrer and reflux condenser were removed and the sodium washed into the reaction flask in a rapid stream of nitrogen, using as a wash the amounts of solvent and halobenzene (a pure grade which had been stored over anhydrous potassium carbonate) which were to be used. The stirrer and condenser were replaced, and the flow of nitrogen was decreased so that the bubble count in the last sulfuric acid wash bottle was between 30-40/min. Stirring was now begun, and the time (A) noted.

In this first preparation 11.5 grams of sodium (0.5 gram atom), 31.4 grams of bromobenzene (0.2 mole), and 200 c.c. of benzene<sup>16</sup> were used. As soon as the stirring was begun the reaction was heated with a free flame to an internal temperature of 44°, and the reactants were held at this temperature by heating until the reaction was enough under way to cause a temperature rise. The time (B) was noted at this point. Time (B) minus time (A) equals the number of minutes required to produce an exothermic effect, or is known as the induction period (35 min.). The reaction temperature was now maintained between 42°-44° by external cooling with a cold water bath until the reaction was no longer exothermic, as evidenced by a drop in temperature. Time (C) is now noted; time (C) minus time (B) equals the exothermic effect period (60 min.). The reaction was then allowed to stir for 45 minutes (standing time), during which time the temperature slowly approached room temperature. After 45 minutes the reaction was heated to between 40°-44° (internal temperature) for two hours by means of a water bath or electric hot plate; this two hour period is known as the stirring period.

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<sup>16</sup>Chemically pure thiophene-free benzene which had been stored over anhydrous calcium chloride.

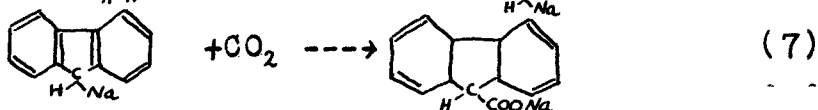
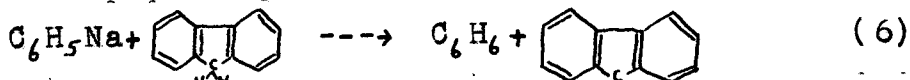
The reaction was now cooled in an ice bath to about  $10^{\circ}$  and diluted with an equal volume of anhydrous, sodium dried ethyl ether. After stirring for about 10 minutes in an ice bath the reflux condenser was replaced by a right angle glass bend and stopper, and the stirrer replaced by a solid stopper. The flask was now removed from the ring stand and tilted so that the stream of nitrogen (which had been stepped up) forced the reaction mixture through the right angle glass bend in jet fashion onto a hand-stirred excess of powdered dry ice in a beaker. Carbonation was thus accomplished in a stream of nitrogen and in small enough portions to avoid excessive splashing caused by the rapid escape of the carbon dioxide. After the carbonation mixture was allowed to warm up to room temperature, it was treated with dilute ethanol (about 100 c.c. of a 75% aqueous solution) to destroy any unreacted sodium and was extracted three times with water. The aqueous extracts were combined, washed once with ether, concentrated to a small volume, filtered with charcoal, and acidified to methyl orange with hydrochloric acid to precipitate any acidic material.

During the induction period black specks were observed and the number increased until at the point of carbonation the reaction mixture was quite black. Upon dilution with ethyl ether there was a heat effect which might well have been due to a heat of solution or the formation of an oxonium complex due to the polarity of the phenyl sodium. The black material insoluble in the ether-benzene solution was probably salt and unreacted sodium. The work-up of this first run yielded 10 grams of benzoic acid (m.p.  $121^{\circ}$ - $122^{\circ}$ ). A mixed melting point with a known sample of benzoic acid showed no depression. Assuming quantitative carbonation, the yield of benzoic acid corresponds to a 40.9% yield of phenyl sodium based on bromobenzene.

A second run of phenyl sodium was made in the same fashion. After the stirring period, however, 24.9 grams of fluorene (twice crystallized from glacial acetic acid - m.p.  $113^{\circ}$ - $114^{\circ}$ ) were added, and the mixture was refluxed with stirring under nitrogen atmosphere for  $4\frac{1}{2}$  hours. Carbonation was carried out in the usual manner to yield 12 grams of fluorene-9-carboxylic acid melting at  $217^{\circ}$ - $222^{\circ}$  with



decomposition.<sup>17</sup> Again assuming quantitative carbonation and also quantitative metalation, this yield corresponds to a 28.57% yield of phenyl sodium based on bromobenzene. The reaction proceeds according to equations (6) and (7).



Increasing the stirring time of the reaction from two to three hours at 43° does not have any significant effect, as shown by run No. 3. In this case the yield of the fluorene acid was 13 grams or equivalent to 30.95% of phenyl sodium. The induction period was unusually long (75 min.) and was attributed to two factors: (1) The sodium had to be powdered a second time and may have become unduly coated; (2) the stirring was accompanied by a good amount of splashing, thus disrupting surface action on the sodium particles. These factors will be discussed in the Appendix (page 25).

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<sup>17</sup> During the work-up of this acid it is unnecessary to concentrate the aqueous alkaline solution. Fluorene-9-carboxylic acid is water insoluble.

It was now decided to observe the effect of raising the temperature limits of the induction, exothermic effect, and stirring periods. Runs No. 4 and No. 5 (using the fluorene method) had a maximum temperature of  $53^{\circ}$  up to the reflux period and yielded 17.5 grams and 17 grams of the fluorene acids, or 41.66% and 40.5% of phenyl sodium respectively. Run No. 6 (without fluorene) under identical conditions gave 8.5 grams of benzoic acid, or a yield of 34.8% phenyl sodium. Runs No. 7 (using fluorene) and No. 8 had a maximum temperature of  $67^{\circ}$  throughout the initial three periods. Respective yields of phenyl sodium were 30.95% and 34.8%, significantly lower than in the two previous runs.

Using now the maximum temperature of  $52^{\circ}$  and increasing the stirring period to three hours, runs No. 9 and No. 10 (using fluorene) gave respective yields of 36.8% and 36.9% phenyl sodium. This would indicate that the additional one-hour stirring is not necessary.

Run No. 11 had a maximum temperature of  $53^{\circ}$ , but the stirring period was shortened to one hour. A 38.9% yield of phenyl sodium was obtained. Run No. 12 had a maximum temperature of  $53^{\circ}$ , a stirring

period of one hour, and the standing time of 45 minutes was eliminated. The yield of phenyl sodium was 32.8%. Eliminating the standing time and restoring the two-hour stirring period (run No. 13) yielded 30.7% phenyl sodium. These results seem to indicate roughly that the elimination of the standing time lowers the yield, while a shortening of the stirring period by one hour has no appreciable effect. This is rather confusing since the temperature decline during the standing time is not great enough to differ considerably from the stirring-period temperature of 53°. Also, and this is true for all the runs that were made of this size, a small difference in yields of benzoic acid (0.5 g) will cause a greater difference in percentage yields of phenyl sodium (2%).

The effect of different temperatures during the initial three periods was now investigated. For example, run No. 14 had a maximum temperature during the induction and exothermic effect period of 67°, while the stirring period was kept at 53°. The result was a 36.8% yield of phenyl sodium. The best yield so far was obtained in run No. 15, during which the induction period was held at 67° and the two ensuing periods were kept at 53°. The yield of

benzoic acid was 11 grams, or about 45.1% phenyl sodium. The acid contained some salt, as was shown by incomplete fusion at 121°. Eliminating the standing time in No. 15 gave a yield of 34.8% phenyl sodium (run No. 16). This latter-type run using fluorene (No. 17) gave a 32.1% yield of phenyl sodium.

Of the series of runs using bromobenzene the results were encouraging (the average yield was 35.76%). Runs No. 1, 4, 5, and 15 were the best. The results would indicate that after the induction period temperatures above 53° have no beneficial effect. The contents of the patent<sup>13</sup> cited in the previous chapter (p. 5) are confirmed by this. The effects from time variations are difficult to interpret, since the total time of reaction must depend on the duration of the induction and exothermic effect periods, which cannot be controlled. These runs are listed in Table I on page 17.

By substituting chlorobenzene for the bromobenzene in run No. 16, run No. 18 yielded 43% phenyl sodium, an 8% improvement. A similar alteration in run No. 17, and also the use of a 90% grade of fluorene<sup>18</sup> (Reilly Tar and Chemical Co. - m.p. 111°-114°),

<sup>18</sup>Contains some phenanthrene, which is not affected by phenyl sodium. The amount used (.15 mole) is an excess.

yielded 40.5% phenyl sodium (run No. 19). This was also an 8% improvement.

Two runs, No. 20 and No. 21, were made similar to No. 19, but substitution of commercial benzene (dried over anhydrous calcium chloride) for the thiophene-free grade was made. Identical yields of 42.9% phenyl sodium were obtained.

TABLE I  
BROMOBENZENE RUNS

Run No.	Ratings Na/Stirt*	Induction Per.		Exothermic Eff. Per.		Stirring Per.		Stand. Time Min.	% C <sub>6</sub> H <sub>5</sub> Na**	Meth-od***
		Min.	°C	Min.	°C	Hrs.	°C			
1	2/1	35	44°	60	44°	2	44°	45	40.9%	B
2	2/1	30	45°	70	45°	2	45°	45	28.6%	F
3	1/1.5	75	43°	75	43°	3	43°	45	30.95%	F
4	1/2	30	53°	90	53°	2	53°	45	41.66%	F
5	3/1	35	53°	50	53°	2	53°	45	40.5%	F
6	3/2	88	53°	60	53°	2	53°	45	34.8%	B
7	3/2	22	67°	30	67°	2	67°	45	30.95%	F
8	3/1	25	67°	30	67°	2	67°	45	34.8%	B
9	1/1	70	52°	53	52°	3	52°	45	36.8%	B
10	3/2	55	52°	55	52°	3	52°	45	36.9%	F
11	1.5/2	58	53°	52	53°	1	53°	45	38.9%	B
12	3/2	68	53°	75	53°	1	53°	0	32.8%	B
13	2/2	70	53°	50	53°	2	53°	0	30.7%	B
14	3/2	30	66°	30	67°	2	53°	45	36.8%	B
15	3/2	33	66°	65	53°	2	53°	45	45.1%	B
16	1/2	20	66°	58	53°	2	53°	0	34.8%	B
17	2/2	55	66°	60	53°	2	53°	0	32.1%	F

\*See Appendix.

\*\*Based on bromobenzene.

\*\*\*F = Fluorene method; B = Benzoic acid method.

It was thought that perhaps a different solvent media might increase the yield. Accordingly run No. 22 was made, in which a purified grade of ethylene glycol diethyl ether<sup>19</sup> was substituted for the benzene. The reaction was immediately exothermic, and the solvent became amber colored. A gas seemed to be given off in small quantities, indicating incomplete purification and dryness or side reactions (ether cleavage by sodium is common). The exothermic effect lasted 45 minutes, at which time the solution was very black and a black sludge settled when the stirring was ceased. After a two-hour stirring at 53°, the reaction mixture was carbonated. The work-up revealed no acidic material.

Run No. 23 was similarly run using dioxane<sup>20</sup> as the solvent. No exothermic effect was noticed after three hours of heating at 67°. At the start of the heating the dioxane turned a deep purple which became increasingly darker. After three hours at 67° fluorene was added, and the reaction was heated at 80°-83° for four and one-half hours, cooled, diluted with ether, and carbonated. The work-up gave 8.5 grams of acid representing 20.2% phenyl sodium.

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<sup>19</sup>Dried over sodium (some gas evolution) and filtered with charcoal.

<sup>20</sup>Dried over sodium and filtered, using charcoal.

The above-mentioned runs are listed in Table II below. The results are self-explanatory.

TABLE II  
CHLOROBENZENE RUNS

Run No.	Induction Per.		Exothermic Eff. Per.		Stirring Per.		Stand. Time Min.	% $C_6H_5Na^a$	Meth-od <sup>b</sup>
	Min.	°C	Min.	°C	Hrs.	°C			
18	20	66°	50	53°	2	53°	0	43.0%	B
19	48	66°	65	53°	2	53°	0	40.5%	F <sup>c</sup>
20	55	66°	45	53°	2	53°	0	42.9%	F <sup>d</sup>
21	47	66°	50	53°	2	53°	0	42.9%	F <sup>d</sup>
22	0	--	45	53°	2	53°	0	0	B <sup>e</sup>
23	0	--	0	--	3	66°	0	20.2%	F <sup>f</sup>

- a. Based on chlorobenzene.
- b. B = Benzoic acid method; F = Fluorene method.
- c. Commercial (90%) grade fluorene used.
- d. Commercial fluorene and benzene used.
- e. Ethylene glycol diethyl ether used as solvent.
- f. Dioxane used as solvent.



## CHAPTER IV

### DISCUSSION AND CONCLUSION

In light of the experimental work, as given in Tables I and II some generalizations are in order. The induction and exothermic effect periods are strictly functions of the reaction itself. Since in general the rate of reaction is directly proportional to the temperature rise, it would be expected to find the times involved in the two periods shortest at the highest temperatures. Such is the case as shown in Table III.

TABLE III

TIME-TEMPERATURE RELATIONSHIP

Run No.	43°	53°	67°	67°-53°
	Min.*	Min.*	Min.*	Min.*
1	95			
2	100			
3	150			
4		120		
9		123		
13		120		
7			52	
8			55	
14			60	
15				98
21				97
20				100
Av.	115	121	55	98

\*Induction period plus exothermic effect period.

Since no time factors are mentioned in the patent<sup>13</sup> referred to previously, it would seem that the recommended 15°-40° reaction range would require considerable time. The same citation states that a 55-75% increase in phenyl sodium yield is obtained by substituting chlorobenzene for bromobenzene. Although the experimental conditions in the patent were slightly different from those followed in this research, only an 8% increase in the phenyl sodium yield was observed.

Many instances occurred during the work when it was impossible to interpret the data accurately. For example, runs No. 7 (with fluorene) and No. 8 differ in phenyl sodium yields by almost 4%, favoring No. 8 and indicating that the fluorene method is less desirable, whereas the almost 6% yield difference in runs No. 5 and No. 6 favor the fluorene method. It is quite possible that such degrees of error may lie in the experimental technique and work-up procedure; and yet, other runs do not bear this out (No. 20 and No. 21 gave identical yields). It was believed that these discrepancies would tend to minimize with larger runs. A series of five runs were then made (procedure as in run No. 19) in which the quantities of

reagents were increased seven times. The phenyl sodium yields ranged from 39.8% to 52.4%. The most significant result is not the persistence or yield variations but the increase of the yield itself. Three of these five runs were better than 49%.

Of interest was a single run made in which the concentration of the reactants in benzene was doubled. The resulting 36.3% yield of phenyl sodium would indicate an advantage when large runs are to be made.

Perhaps the most plausible reason for the inconsistencies that have occurred is the great number of variables involved. In many cases it was difficult to have only one quantity as a variable, and when more than one variable was present the results could not be accurately understood.

The purpose of this investigation, it is felt, has been fulfilled. Consistent yields of between 40-50% phenyl sodium have been obtained by means of a short and convenient method.

The following modifications have been made in the initial procedure:

1. The temperature of the induction period was changed from 43° to 67°.

2. The temperature of the exothermic effect and standing periods was changed from 43° to 53°.
3. The forty-five minute standing time is not necessary.
4. In large runs the concentration may be increased without greatly lowering the yield.

## BIBLIOGRAPHY

The bibliography includes all of the periodical chemical literature up to the year 1942. In addition, the chapter on organometallic compounds found in Henry Gilman's book, "Organic Chemistry" (John Wiley and Sons, New York, Vol. I, pp. 406-89) was very helpful.

Every significant article that has been used has been recorded in the footnotes of this thesis.

## APPENDIX

### SODIUM

It was thought at the outset of this study that the physical condition of the sodium powder would have a direct bearing on the course of the reaction. The long induction period in run No. 3 was partly attributed to the sodium in a low state of reactivity (coated particles being obtained because of undue exposure during the powdering procedure). A rough numerical rating was then given to each succeeding quantity of powdered sodium as follows:

3 = very finely powdered with only a few unduly large particles.

2 = about  $2/3$  fine powder and  $1/3$  large particles.

1 = twice powdered, hence a greater opportunity for atmospheric corrosion.

These ratings are listed in Table I. Such ratings were expected to show that the onset of the reaction was dependent upon the amount of sodium exposed. It was also assumed that the finer the particles of sodium the greater would be the amount exposed. Con-

sidering those runs which had the same induction period temperature, it is seen that uniform results do not occur. For example, runs Nos. 5, 6, 10, and 12, having sodium ratings of 3, had respective induction periods (at 53°) of 35, 88, 55, and 68 minutes. Runs Nos. 9, 11, and 13, having lower ratings, had induction periods (at 53°) of 70, 58, and 70 minutes respectively. Due, perhaps, to the large number of variables present, significant results are probably only available by a statistical method which necessitates large numbers of runs.

#### STIRRING

The meanings ascribed to the stirring ratings listed in Table I are:

2 = rapid circular motion with very little splashing.

1 = rapid circular motion with a fair amount of splashing.

$\frac{1}{2}$  = rapid circular motion with a good deal of splashing.

It was believed that splashing might effectively shorten the contact time of the halobenzene with the sodium and hence increase the induction and exothermic effect periods. It is sufficient to say that no correlation could be recognized with the number of runs that were made and that, as with the case of the attempted sodium ratings, significant results may only occur when a relatively large number of runs are made.