

1940

Lateral organoalkali compounds

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LATERAL ORGANOALKALI COMPOUNDS

by

Henry Alexander Pacevitz

LAST NAME CHANGED TO *PACE*
BY COURT ORDER IN 1943
AKRON, OHIO

**A Thesis Submitted to the Graduate Faculty
for the Degree of**

DOCTOR OF PHILOSOPHY

Major Subject Organic Chemistry

Approved:

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In charge of Major work

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1940**

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I. INTRODUCTION

The increasing dependence of synthetic organic chemistry on organometallic compounds stimulated this investigation of the selective metalation of side chains attached to various aromatic nuclei.

Often, in the course of an original investigation, many problems arise which subsequently prove to be of general value to the field as a whole. Such problems exposed themselves and were attacked with as much vigor as the original objective.

The problem of increasing the length of carbon chains has always been of fundamental importance. As a rule the organometallic compound which is required in this process originates directly from the halogen compound. In certain cases the desired halide is not readily available and much time is lost in its preparation and purification. Lateral metalation is a tool by which the desired organometallic can be produced from the more readily available parent hydrocarbon of the halide and a common halogen compound, such as chlorobenzene, in combination with either sodium or potassium metal.

A phenomenon of the migration of the alkali atom from the nucleus to the side chain was observed and upon further

study proved to be another useful method of effecting a lateral metalation.

The rate of carbonation of lateral organometallics was found to be of very significant importance with regard to the nature of the product which was formed. The extensive carbonation experiments quite definitely excluded certain erroneous ideas which were being imbedded in the realm of organoalkali chemistry.

Later sections of the experimental part of this thesis include work on interconversion reactions and the allylic rearrangement.

It is true that the chemistry of organoalkali compounds is somewhat hazardous, but this inconvenience is readily removed by rigorously adhering to all common principles of precaution and technique.

II. HISTORICAL

A. Preparation of Lateral Organoalkali Compounds

Some of the most widely studied organometallic compounds are those having an alkali metal attached to a side chain which is attached to an aromatic nucleus and are known as lateral organoalkali compounds. Certain organoalkali compounds, such as those of fluorene, are not considered to be in this class of substances since the reactive hydrogen atom is attached to a carbon atom which is part of a cycle instead of a side chain as is specifically defined.

The properties of lateral organoalkali compounds, with a few exceptions, are those common to most organometallic compounds. However, the methods of preparation are quite varied and a very great number of compounds result from these methods. Therefore, in this case, a clear historical discussion can be obtained only by discussing each of the organoalkali compounds according to a sequence of preparations. The sequence is initiated with the simple replacement reaction of a hydrogen atom by a metal and leads up to the more recent method which involves the migration of the alkali metal within the molecule.

The discussion on the reactions of the lateral organo-alkali compounds is segregated and occurs directly after the main body of the discussion on the methods of preparing these compounds. This division was made in order to attempt generalizations and eliminate repetition.

1. Replacement of hydrogen with alkali metal.

The simplest method of preparing lateral organoalkali compounds is by the replacement of a hydrogen atom with an alkali metal. The highly acidic nature of the acetylenic hydrogen atom in phenylacetylene was used by Glaser¹ to prepare phenylethynylsodium by reacting the hydrocarbon with sodium metal in diethyl ether.

Young² found that potassium, rubidium and cesium, but not lithium, reacted with phenylacetylene to yield compounds corresponding to the one obtained by Glaser¹ as was evidenced by the formation of phenylpropionic acid, subsequent to carbonation, in each case.

The least complex of the more heavily arylated methane hydrocarbons to undergo substitution is diphenylmethane. Sodium suspended in organic solvents had no action upon this hydrocarbon,³ but a reaction did occur when the

1. Glaser, Ann., 154, 161 (1870).

2. Gilman and Young, J. Org. Chem., 1, 315 (1936).

3. Schlenk, in Houben-Weyl, "Die Methoden der Organischen Chemie", Vol. IV, pp. 945-978, George Thieme, Leipzig (1924).

organic liquids employed as solvents in the experiment were replaced by liquid ammonia.⁴ When potassium was used in the absence of a solvent, a reaction occurred between the metal and diphenylmethane on heating the reactants to a temperature of 230° to give the dipotassium compound, $(C_6H_5)_2CK_2$, as the product.⁵

Hanriot and Saint-Pierre⁶ heated triphenylmethane with potassium metal in an inert atmosphere and observed the formation of a red substance which they assumed to be triphenylmethylpotassium. Since then it has been shown that their assumption was correct. Triphenylmethylsodium was prepared by Kraus and Kawamura⁷ by the action of sodium on triphenylmethane in liquid ammonia. Triphenylmethane reacted with sodium-amalgam but not with sodium in organic solvents;⁸ however, cesium and rubidium react with the hydrocarbon in such media.⁹ Potassium reacted readily with triphenylmethane^{4b,6} when the two were heated to a temperature of 240°.

That there is no danger of metalating the aromatic nucleus is found in the following sequence of work.

-
4. (a) Lebeau and Picon, Compt. rend., 173, 84 (1921); (b) Wooster and Mitchell, J. Am. Chem. Soc., 52, 688 (1930).
 5. Saint-Pierre, Bull. soc. chim., [3], 5, 292 (1891).
 6. Hanriot and Saint-Pierre, ibid., [3], 1, 774 (1889).
 7. Kraus and Kawamura, J. Am. Chem. Soc., 45, 2756 (1923).
 8. Schlenk and Holtz, Ber., 49, 603 (1916).
 9. v. Grosse, ibid., 59, 2646 (1926).

Abeljanz¹⁰ reported the metalation of benzene with potassium when heated to a temperature of 240-250° over a period of seven days. He postulated that the product was a mixture of phenylpotassium and phenylenedipotassium. Schlenk¹¹ repeated the work, finding that the supposed phenylpotassium was, in reality, potassium with an insoluble black coating. Hackspill¹² prepared phenylcesium by the direct action of the very reactive metal upon benzene, but in view of Schlenk's contradiction of Abeljanz's work this result should be verified by an independent worker.

The intense activity of the acetylenic hydrogen atoms is further indicated by the work of Conant¹³ wherein indenylsodium, a very weak metalating agent, was used to replace the hydrogen of phenylacetylene to form phenylethynylsodium. Young² has prepared phenylethynyllithium by metalating the corresponding hydrocarbon with phenyllithium and n-butyllithium and states that, in all probability, this can be accomplished by using any organolithium compound derived from a hydrocarbon containing a lesser acidic hydrogen than phenylacetylene.

10. Abeljanz, ibid., 9, 10 (1876).

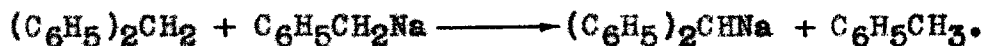
11. Schlenk and Meyer, ibid., 46, 4060 (1913).

12. Hackspill, Ann. chim., 7 8, 28, 653 (1913).

13. Conant and Wheland, J. Am. Chem. Soc., 54, 1212 (1932).

2. Metalation of hydrocarbons with organoalkali compounds.

According to Schlenk¹⁴ diphenylmethylsodium is best prepared by a double decomposition reaction, using diphenylmethane and benzylsodium,



The product is orange-red and stable in diethyl ether. The reaction was allowed to proceed, with shaking, for a period of five to six days during which the diphenylmethylsodium precipitated¹⁴ as an orange-red solid. Phenylsodium has been employed to metalate this hydrocarbon¹⁵ in benzene solution, the lateral position of the sodium atom being proved by the usual carbonation method. No yields were given to indicate the extent of the metalation. Diphenylmethane was also metalated by Kirby¹⁶ when he treated the hydrocarbon with an ether solution of n-butyllithium for twenty hours and then obtained a 20% yield of diphenylmethylsodium as evidenced by the formation of diphenylacetic acid on carbonation.

Triphenylmethylpotassium, -sodium and -lithium were prepared by Young² in ether solution from triphenylmethane, di-n-butylmercury and the corresponding alkali metal.

14. Schlenk and Bergmann, Ann., 464, 18 (1928).

15. Böckmühl and Ehrhart, German patent, 671,098 (1939) [C.A., 33, 3391 (1939)]; Böckmühl and Ehrhart, German patent, 633,083 (1936) [C.A., 30, 7582 (1936)]

16. Kirby, R. H., Unpublished observations.

Triphenylmethyl lithium was also obtained from the hydrocarbon and *n*-butyllithium prepared in accordance with the method of Gilman and co-workers.¹⁷

A delayed publication of some work by Dr. R. V. Young¹⁸ revealed that phenylisopropylsodium may be prepared in 41% yield, by the reaction of diethylmercury and sodium using cumene as the solvent.

While studying the conditions of structure necessary for the addition of organoalkali compounds to ethylenic linkages, Ziegler and co-workers¹⁹ found that certain members of the phenylated ethylenic derivatives would undergo substitution reactions (or metalation) rather than addition of the organometallic compounds. It was noted that the addition reactions, when they did occur, were almost instantaneous in rate while the substitution reactions took place only over varying periods of time. As an example, $(C_6H_5)_2C=CHCH_3$ reacted completely with phenylisopropylpotassium in one hour, while a closely related compound $(C_6H_5)CH=C(CH_3)_2$ required twenty-four hours for metalation. An indication of the variety of compounds preparable by this substitution reaction is given in Table I.

17. Gilman, Zoellner and Selby, J. Am. Chem. Soc., 54, 1957 (1932).

18. Gilman, Pacevitz and Baine, ibid., 62, 1519 (1940).

19. Ziegler, Crössmann, Kleiner and Schäffer, Ann., 473, 1 (1929).

TABLE I

Substituted Ethylenes Metalated by Phenylisopropylpotassium

<u>Compound metalated</u>	<u>Compound formed</u>
$(C_6H_5)CH=C(CH_3)_2$	$(C_6H_5)CH=C(CH_3)CH_2K$
$(C_6H_5)_2C=CHCH_3$	$(C_6H_5)_2C=CHCH_2K$
$(C_6H_5)_2C=C(CH_3)_2$	$(C_6H_5)_2C=C(CH_3)CH_2K$ and $(C_6H_5)_2C=C(CH_2K)_2$
$(C_6H_5)_2C=CHCH_2CH_3$	$(C_6H_5)_2C=CHCH(K)CH_3$
$(C_6H_5)_2C=CHCH_2(C_6H_5)$	$(C_6H_5)_2C=CHCH(K)(C_6H_5)$
$(C_6H_5)(CH_3)C=CH(C_6H_5)$	$(C_6H_5)_2CH_2(K)C=CH(C_6H_5)$
$(C_6H_5)CH_2CH=CHCH_2(C_6H_5)$	$(C_6H_5)CH(K)CH=CHCH_2(C_6H_5)$ and $(C_6H_5)CH(K)CH=CHCH(K)(C_6H_5)$
$(C_6H_5)CH_2(CH=CH)_2CH_2(C_6H_5)$	$(C_6H_5)CH(K)(CH=CH)_2CH(K)(C_6H_5)$

Schorigin²⁰ first observed the process of later metalation in his studies on ethylsodium, prepared from diethylmercury and sodium, as a metalating agent. After isolating benzoic acid subsequent to the carbonation of a benzene suspension of ethylsodium, he tried this transference effect on toluene, a nucleus which affords the possibility of either nuclear or lateral metalation. It was found that when the ethylsodium was prepared from diethylmercury in the presence of toluene, only phenylacetic acid resulted. Surprisingly however, when the ethylsodium was prepared

20. Schorigin, Ber., 41, 2723 (1908).

from diethylzinc in toluene, the phenylacetic acid was contaminated with *p*-toluic acid. Several other methylated benzenes were employed as solvents. When *m*-xylene and ethylbenzene were used, *m*-tolylacetic and hydratropic acids were obtained, respectively. In the case of the ethylbenzene it is interesting to note that metalation occurred on the α -carbon atom rather than in the terminal group.

In further researches, Schorigin²¹ extended his work to metalation of other nuclei, with subsequent carbonation and isolation of the corresponding acids as a measure of the extent of metalation. The following table gives a summary of the nuclei which were exposed to the metalating effects of ethylsodium and the results obtained.

TABLE II

Yields of Acids from the Various Nuclei after Metalation

<u>Nucleus employed</u>	<u>Acid isolated</u>	<u>Yield (%)</u>
Diphenylmethane	Diphenylacetic acid	0.9
Phenylethane	Hydratropic acid	1.0
<i>p</i> -Xylene	<i>p</i> -Tolylacetic acid	3.3
<i>m</i> -Xylene	<i>m</i> -Tolylacetic acid	8.0
Toluene	Phenylacetic acid	16.0
<i>o</i> -Xylene	<i>o</i> -Tolylacetic acid	16.6
Mesitylene	<i>s</i> -Dimethylphenylacetic acid	18.3
<i>p</i> -Cymene	<i>p</i> -Homocumic acid	2.2

21. Schorigin, *ibid.*, 43, 1938 (1910).

These extensive experiments by Schorigin led him to the formulation of a statement which is now known as the Schorigin Rule:²¹ "In metalation, the carboxyl group enters a position such that the resultant acid has the lowest melting point with respect to all other isomers." This rule does not apply to the nuclear metalations of dibenzothiophene²² but does seem to hold quite well in the case of the closely related oxygen analog, dibenzofuran,²³ when metalated by organoalkali compounds. One of the few exceptions found in the literature to this rule is located in a paper by Gilman²⁴ upon the metalation of 2-methylfuran. A nuclearly substituted product was isolated, although the melting points of the isomers (α -furylacetic acid, 68°; 5-methyl-2-furoic acid, 109°) suggests that furylacetic acid should have been formed. This exception, however, does not disprove the rule, especially since allylic rearrangements are known to occur in reactions involving the 2-furylmethyl radical.²⁵

Deviating for an instant to mercurials, it was observed that while the metalation of toluene with organoalkali compounds involved the side chain predominantly, metalation

-
22. Gilman and Jacoby, *J. Org. Chem.*, 3, 108 (1938); Gilman, Jacoby and Pacevitz, *ibid.*, 3, 120 (1938).
23. Gilman and Young, *J. Am. Chem. Soc.*, 56, 1415 (1934); Gilman and Young, *ibid.*, 57, 1121 (1935); Gilman, Cheney and Willis, *ibid.*, 61, 951 (1939); Gilman and P. R. Van Ess, *ibid.*, 61, 1371 (1939); Gilman, Langham and Willis, *ibid.*, 62, 346 (1940).
24. Gilman and Breuer, *ibid.*, 56, 1123 (1934).
25. Runde, Scott and Johnson, *ibid.*, 52, 1284 (1930).

with mercury compounds placed the metal upon the nucleus.²⁶

Morton,²⁷ upon the preparation of n-amylsodium from di-n-amylmercury in toluene solution, obtained, subsequent to carbonation, phenylacetic acid (13%) and phenylmalonic acid (45%). The work on this metalation of toluene has been extended and a complete discussion may be found on page 144.

Gilman and Bebb,²⁸ observed that lateral metalation of diarylmethanes appears to be affected significantly by the nature of the aryl group. When n-butyllithium was used as the metalating agent, the yield of diphenylacetic acid from diphenylmethane was 20%; the yield of phenyl-p-tolylacetic acid from phenyl-p-tolylmethane was 50%; and the yield of phenyl- α -naphthylacetic acid from phenyl- α -naphthylmethane was 80%. Bibenzyl was laterally dimetalated by n-butylsodium and n-butylpotassium, in benzene, to an extent of 50% and 52%, respectively. The product obtained after carbonation was α,β -diphenylsuccinic acid.

3. Metalation with sodium amide.

According to the work of Wooster,²⁹ sodium amide does not metalate diphenylmethane in organic solvents. However,

26. Dimroth, Ber., 31, 2154 (1898); 32, 758 (1899); 35, 2032 (1902).

27. Morton and Hechenbleikner, J. Am. Chem. Soc., 58, 1024 (1936).

28. Gilman and Bebb, ibid., 61, 110 (1939).

29. Wooster, Chem. Rev., 11, I (1932).

on changing the reaction medium from an organic solvent to liquid ammonia, the reaction proceeds smoothly with the formation of diphenylmethylsodium as the product.^{4b}

In an attempt to prepare alkyl- and phenylalkali compounds in liquid ammonia, investigators³⁰ obtained unsuccessful results due to the ammonolysis of the organoalkali compounds as soon as they were formed. It might be said, then, that in these cases the ionization of the hydrocarbon is less than that of the ammonia. On the other hand, when the hydrocarbon is ionized to an extent greater than that of ammonia, the formation of the organometallic compound may be successfully completed in that solvent. Wooster and Mitchell^{4b} investigated various phenylated methanes and ethanes, observing their reactivity toward sodium amide, potassium amide and potassium in liquid ammonia. Observation of the results, indicated in Table III, led to the formulation of the "Benzohydryl Rule".^{4b} "The ability of potassium amide to replace with a potassium atom a hydrogen atom in a hydrocarbon of this class is confined to those compounds in which at least two phenyl radicals are attached to a single carbon atom. Even then, reaction takes place only when this carbon atom holds a hydrogen attached to it in addition to the two phenyl

30. Kraus and White, *J. Am. Chem. Soc.*, 45, 777 (1923);
White, *ibid.*, 45, 779 (1923).

groups. It is this particular hydrogen which is involved in the metalation, being the one replaced by the potassium."

TABLE III

Action of Potassium and Potassium Amide on Phenylated Methanes and Ethanes

<u>Compound metalated</u>	<u>Potassium</u>	<u>Potassium amide</u>
$C_6H_5CH_3$	No action	No action
$(C_6H_5)_2CH_2$	Reacts	Reacts
$(C_6H_5)_3CH$	Reacts	Reacts
$(C_6H_5)_4C$	No action	No action
$C_6H_5CH_2CH_3$	No action	No action
$C_6H_5CH_2CH_2C_6H_5$	No action	No action
$(C_6H_5)_2CHCH(C_6H_5)_2$	Reacts	Reacts
$(C_6H_5)_2CHCH_2C_6H_5$	Reacts	Reacts
$(C_6H_5)_3CCH_3$	Slight reaction	No action
$(C_6H_5)_3CCH_2C_6H_5$	Slight reaction	No action
$(C_6H_5)_3C-C(C_6H_5)_3$	Cleaves and then adds	-----

Triphenylmethylsodium may be readily prepared in a very pure state by reacting triphenylmethane with sodium amide in liquid ammonia.

4. Addition of metal to free radical.

In general, the triarylmethylalkali compounds may be prepared by the action of an alkali metal on an ethereal solution of the free radical.

According to Schlenk and Marcus^{31a} sodium does not add to triphenylmethyl in ether except in the form of sodium-amalgam; instead the radical is polymerized to p-benzohydryltetraphenylmethane under the influence of the sodium metal. However, under the conditions of Bachmann and Wiselogle,^{31b} wherein the surface of the sodium metal was kept clean by stirring with glass beads, the triphenylmethyl and sodium reacted rapidly in ether to give triphenylmethylsodium in practically quantitative yields, only traces of the dimer being formed. p-Biphenyl- α -naphthylphenylchloromethane when treated with copper powder and sodium metal in ether solution gives p-biphenyl- α -naphthylphenylmethylsodium. Di-p-biphenyl- α -naphthylchloromethane yields di-p-biphenyl- α -naphthylmethylsodium when treated in the same manner.^{31a}

5. Replacement of halogen with metal and also amalgam.

Triphenylchloromethane was found to react very readily with sodium-amalgam^{31a,32} in organic solvents to give

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31. (a) Schlenk and Marcus, Ber., 47, 1664 (1914); (b) Bachmann and Wiselogle, J. Am. Chem. Soc., 58, 1943 (1936).
32. Schlenk and Ochs, Ber., 49, 608 (1916).

triphenylmethylnsodium.

Curiously enough, the best reaction to use for preparing triphenylmethylnsodium is one that a number of investigators³³ have concluded as being negative. They stated that sodium did not react with either triphenylchloromethane or triphenylbromomethane in ether or benzene. However, Bachmann and Wiselogle^{31b} found that triphenylchloromethane reacted rapidly with sodium in ether solution to give nearly quantitative yields of triphenylmethylnsodium, provided the surface of the sodium was kept exposed. It was decided that sodium chloride which forms on the surface of the sodium stopped the reaction and caused the discrepancy in the results obtained. This reaction also occurs in benzene solution but at a much slower rate.

von Grosse⁹ prepared triphenylmethylpotassium, -lithium, -rubidium and -cesium by use of triphenylchloromethane, the corresponding metal-amalgam, and in an anhydrous ether solution. Rubidium and cesium reacted with triphenylchloromethane in organic solvents. All of these substances are intensely red solids, soluble in ether and in benzene. The sodium and potassium compounds have also been shown to be soluble in liquid ammonia and to conduct the electric current in solution.³⁴

33. (a) Morton and Stevens, J. Am. Chem. Soc., 54, 1919 (1932); (b) Elbs, Ber., 17, 700 (1884); (c) Gomberg, ibid., 33, 3150 (1900).

34. Kraus and Rosen, J. Am. Chem. Soc., 47, 2739 (1925).

β -Styryllithium³⁵ has been prepared by reacting β -bromostyrene and lithium in ether.

Mr. F. W. Moore, of these laboratories, has been unable to verify the statement of Ziegler³⁶ that benzyl chloride reacts with lithium in ether to give bibenzyl. No reaction was observed. Benzyl bromide and also benzyl chloride did not react with lithium in ligroin, even when allowed a reaction time of six weeks.³⁷

Benzylsodium and benzylpotassium have been prepared by the action of the corresponding alkali metals on benzyl halides in liquid ammonia solution.^{4b,30} A deep red color developed in each case, and this gradually faded until the solution was colorless. It was concluded that the red color was due to the benzylalkali compounds. However, it is obvious that this is not a suitable method for preparing these compounds.

6. Metal halyls.

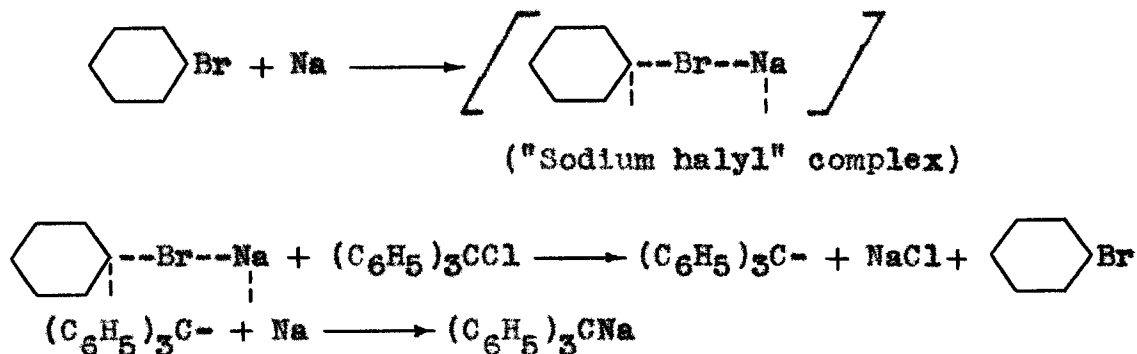
In 1932, Morton and Stevens^{33a} prepared triphenylmethylsodium by the action of sodium on triphenylchloromethane in diethyl ether with the aid of "metal halyls". These substances are assumed to be formed when either

35. Wright, *J. Org. Chem.*, 1, 457 (1936).

36. Ziegler and Dersch, *Ber.*, 64, 448 (1931).

37. See page 67 of this thesis.

bromobenzene, chlorobenzene, n-butyl chloride, benzophenone or tetraphenylethylene is added to the reaction mixture of triphenylchloromethane and sodium according to the following mechanism:



Dr. R. V. Young² substituted triphenylmethane for the triphenylchloromethane with successful results.

7. Displacement reactions.

The simplest representatives of the colored organo-alkalis are the benzylalkali compounds. Ziegler and Dersch³⁶ prepared benzyl lithium by shaking an ether solution of benzylmagnesium chloride with lithium for two to three days. The magnesium was displaced by the lithium according to the following reaction:



This reaction is quite slow and unless time and dilution factors are carefully controlled no benzyl lithium, or only a very small yield, will be obtained.

Benzylsodium may be prepared in the pure state by the interaction of dibenzylmercury and sodium in benzene solution.³⁸ As the brick-red organoalkali compound forms it precipitates from the benzene or petroleum ether solution. It may be redissolved in diethyl ether but the solution must be kept very cold or the ether will be cleaved immediately. Even the cold, reddish-yellow ether solution, which is capable of conducting the electric current, decomposes quite rapidly. In this respect it differs very greatly from the corresponding lithium compound which is quite stable in ether. Benzylsodium is inflammable in air and forms large amounts of stilbene when oxidized very slowly.³⁸

No sodium or potassium derivatives of vinyl or substituted vinyl radicals are known. An attempt³⁹ to prepare $(C_6H_5)_2C=CHNa$, diphenylvinylsodium, from the corresponding mercurial resulted in the formation of 1,1,4,4-tetraphenylbutene-2-disodium-1,4, $(C_6H_5)_2CNaCH=CHCNa(C_6H_5)_2$.

8. Halogen-metal interconversions.

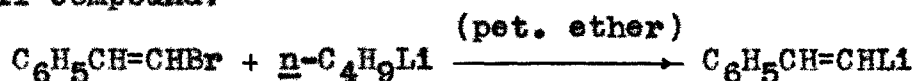
Gilman and co-workers⁴⁰ observed that when β -bromostyrene and n-butyllithium were heated in petroleum ether

38. Schlenk and Holtz, Ber., 50, 262 (1917).

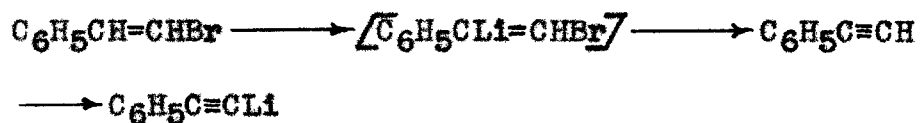
39. Schlenk and Bergmann, Ann., 463, 98 (1928).

40. Gilman, Langham and Moore, J. Am. Chem. Soc., 62, 2328 (1940).

(b.p., 35-50°) for twenty hours and then carbonated, a 23% yield of trans-cinnamic acid resulted. The yield after heating for but one hour was 19%. This preparation of β -styryllithium by a halogen-metal interconversion is one of the most recent methods of preparing a lateral organo-alkali compound:



When diethyl ether was used as the medium, the reaction between the β -bromostyrene and n-butyllithium took a different course inasmuch as a 42.5% yield of phenylpropionic acid was obtained on carbonation. One of the mechanisms offered for this reaction involves a lateral organoalkali intermediate which has not been established up to the present time:



9. Metal-metal interconversion.

Metal-metal interconversion serves as the best method known at the present time for the preparation of benzyl-lithium. This benzylalkali compound may be obtained by the action of phenyllithium and also lithium alkyls on dibenzylmercury^{38,41} according to the following reaction:

41. Hein, Petzchner, Wagler and Segitz, Z. anorg. allgem. Chem., 141, 204 (1924).



Benzylmagnesium chloride reacts with phenyllithium³⁸ and according to the investigators this is the most convenient method of preparing solutions of benzyl lithium for use in reactions where the presence of the diphenylmagnesium affords no disadvantage.



A method of preparing benzyl lithium which is quite identical with that of Hein and co-workers,⁴¹ except for the much more convenient method of preparing the alkyl-alkali from n-butyl bromide and lithium in place of the more expensive diethylmercury, was used by Ziegler.⁴² This reaction is the one that Ziegler¹⁹ used in order to determine the amount of organolithium compound present in ether solution, namely, the interconversion of dibenzylmercury with n-butyllithium.

10. Cleavage reactions.

Cleavage reactions may be used to prepare lateral organoalkali compounds but usually the compounds necessary in these reactions are difficult to obtain, and the yields, as a rule, are not good. Marcus,⁴³ in some studies with

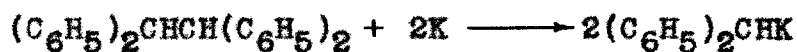
42. Ziegler and Schäffer, Ann., **511**, 13 (1934).

43. Marcus, E., Dissertation: "Beiträge zur Kenntnis der Triarylmethyle," Thomas and Hubert (Weida i. Th.), Jena, 1914. Original not seen. Cited: Jahresverzeichnis der an den Deutschen Universitäten Ershienenen Schriften, **30**, 663 (1914).

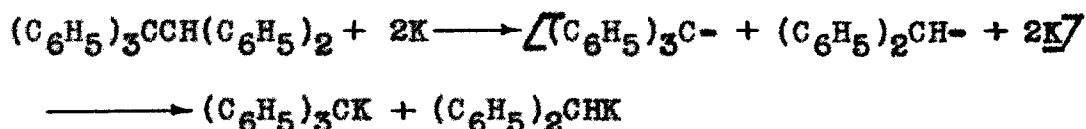
Schlenk, mentioned that 1,1,1,2-tetraphenylethane was cleaved by potassium to triphenylmethylpotassium and benzylpotassium.



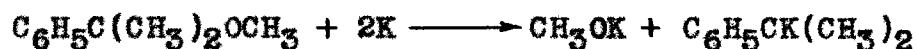
Subsequently, Ziegler and Thielmann,⁴⁴ in an orienting experiment, carried out a similar reaction with sodium-potassium alloy and isolated, after carbonation, triphenylacetic acid but no phenylacetic acid. Diphenylmethylalkali compounds may be conveniently prepared from the methyl ether of benzohydrol and also from sym-tetraphenylethane by cleavage with sodium-potassium alloy.⁴⁴



Schlenk and Marcus^{31a} treated pentaphenylethane with potassium metal and obtained triphenylmethylpotassium and diphenylmethylpotassium according to the following mechanism:



The cleavage of the methyl ether of dimethylphenylcarbinol is used as a method of preparing phenylisopropylpotassium.⁴⁵



These cleavage reactions are of interest not only for preparing organoalkali compounds but also may be used as a

44. Ziegler and Thielmann, Ber., 56, 1740, 2453 (1923).

45. Ziegler and Schnell, Ann., 437, 227 (1924).

test for weakened carbon to carbon bonds.

Koelsch and Rosenwald⁴⁶ reported an interesting case in which lithium apparently cleaved a carbon to carbon linkage. 1,1,3,3,3-Pentaphenyl-1-propene and lithium in ether, after several days, gave on hydrolysis triphenylmethane and 1,1,4,4-tetraphenyl-2-butene. Carbonation yielded triphenylacetic acid and 1,1,4,4-tetraphenyl-1,4-dicarboxy-2-butene. These results indicated that the pentaphenylpropene split into two parts, a triphenylmethyl radical and a 2,2-diphenylethenyl radical, the latter dimerizing either before or after addition of lithium to form the substituted butene.

11. Addition of alkali metals to unsaturated linkages.

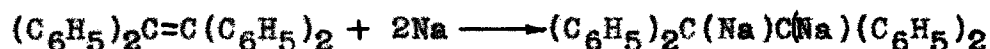
Schlenk and co-workers observed a reaction involving the addition of alkali metals to various phenylated hydrocarbons.⁴⁷ Generally, this type of addition occurred when the carbon atoms of the unsaturated group were "loaded" with ether phenyl, naphthyl and biphenyl groups. There are a few cases in which there is an addition to the double bond^{47a} when no aromatic groups are present, but since this addition does not involve lateral aromatic compounds, it will not be discussed.

46. Koelsch and Rosenwald, J. Am. Chem. Soc., 59, 2170 (1937).

47. (a) Schlenk, Appenrodt, Michael and Thal, Ber., 47, 473 (1914); (b) Schlenk and Bergmann, Ann., 463, 1 (1928).

These particular reactions are not very rapid and a single unsaturated compound may give rise to a variety of products. Some molecules, however, give well defined products which are usually identified by forming known derivatives. Aside from the normal or simple addition of alkali metal, there also occur dimerizing and disproportionation additions. Examples of each of these various kinds of addition follow:

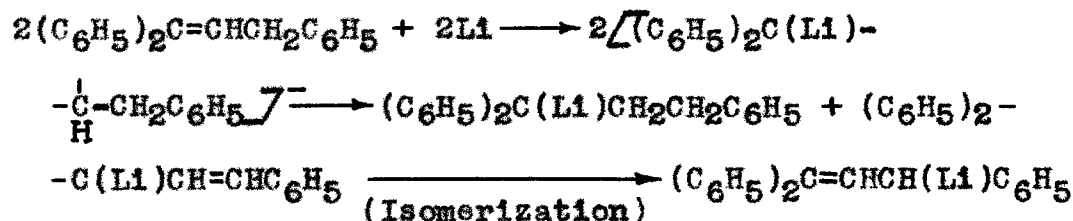
I Normal addition



II Dimerizing addition

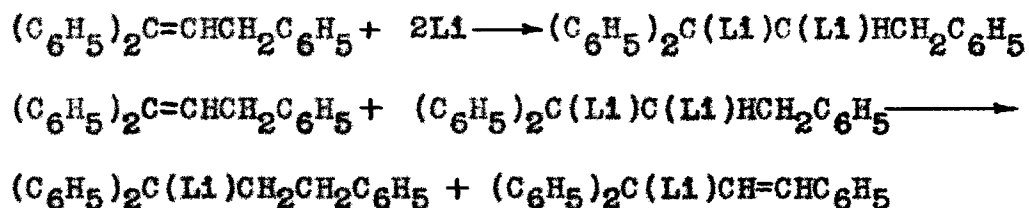


III Disproportionation addition



In example III it may be seen that two free radicals disproportionate to give a saturated and unsaturated hydrocarbon. However, K. Ziegler suggested that this reaction can occur without the formation of the two free radicals in the following manner:⁴⁸

48. Schlenk and Bergmann, *ibid.*, 479, 42, 58, 78 (1930).



Similar reactions have been observed with potassium. Occasionally lithium reacts more rapidly than sodium, but in the large number of hydrocarbons investigated,^{47b} lithium generally acted more slowly. The organopotassium compounds were usually prepared in petroleum ether while the sodium and lithium compounds were generally prepared in diethyl ether. The use of petroleum ether for the organopotassium compounds is indicative of increased activity and emphasizes the precaution that is necessary in choosing solvents for the more reactive organometallic compounds.

Schlenk and Bergmann⁴⁸ compiled the following table showing the addition of alkali metals to various unsaturated hydrocarbons.

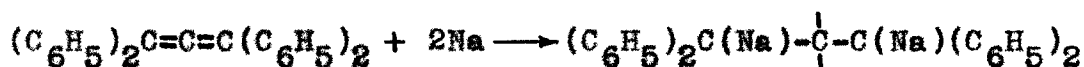
TABLE IV

The Addition of Alkali Metals to the Carbon-Carbon Double Bond

<u>Compound</u>	<u>Addition product</u>
$(C_6H_5C_6H_4)_2C=CH_2$	$(C_6H_5C_6H_4)_2C(Na)CH_2CH_2C(Na)(C_6H_4C_6H_5)_2$
$(C_6H_5)_2C=CHC_6H_5$	$(C_6H_5)_2C(Na)CH(Na)C_6H_5$
$(C_6H_5)_2C=C(CH_3)C_6H_5$	$(C_6H_5)_2C(Na)C(Na)(CH_3)C_6H_5$
$(C_6H_5)_2C=CHCH_3$	No reaction
$(C_6H_5)_2C=C(CH_3)_2$	No reaction with sodium $(C_6H_5)_2C(Li)C(CH_3)=CH_2(?)$
$C_6H_5CH=C(CH_3)_2$	No reaction
$C_6H_5(CH_3)C=C(CH_3)_2$	No reaction
$(C_6H_5)_2C=C(CH_2C_6H_5)_2$	No reaction
$(C_6H_5)_2C=CHCH_2C_6H_5$	Substitution: $(C_6H_5)_2C(Na)CH=CHC_6H_5(?)$
$(C_6H_5)_2C=CHCH(C_6H_5)_2$	Complex reaction
$(C_6H_5)_2C=C(CN)C_6H_5$	$(C_6H_5)_2C(Na)C(Na)(CN)C_6H_5$

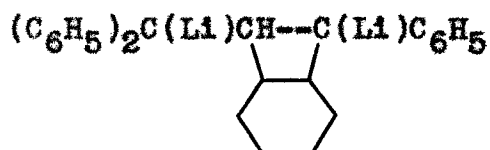
A few cases⁴⁹ have been observed in which only two atoms of alkali metal added to the allenic linkage. In this reaction both double bonds were cleaved, the result being an arylated derivative of methylene having an apparent divalent carbon atom.

49. Schlenk and Bergmann, Ann., 463, 228 (1928).



The red bis- $\sqrt{\text{diphenylmethylsodium}}$ -methylene formed.

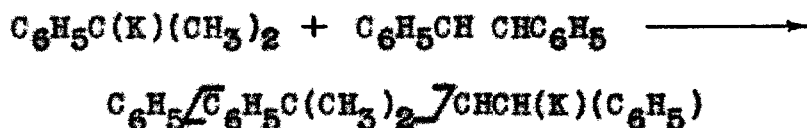
Lithium, on the other hand, reacted to give the following compound:



Referring to the normal addition of alkali metals to tetraphenylethylene, it is well known that sodium adds quite readily,⁴⁷ this being true only of sodium. Lithium does not add under corresponding conditions and this is not surprising in view of its lesser general reactivity. Likewise, potassium apparently does not add, and the positive reaction with sodium-potassium alloy may have been due to the initial addition of sodium followed by replacement of the two sodium atoms with potassium. Rubidium and cesium also do not add. Sodium-rubidium alloy gave the rubidium compound while the behavior of sodium-cesium alloy was not reported. The apparent lesser reactivity of these otherwise extremely reactive metals may be due to steric factors; in the case of tetraphenylethylene there is present a highly sterically hindered olefinic linkage, and this together with the relatively large atomic volumes of the rubidium and cesium atoms may combine to prohibit addition.²

12. Addition of organoalkali compounds to unsaturated linkages.

The first addition of organoalkali compounds to unsaturated linkages was observed by Ziegler⁵⁰ in the case of the addition of phenylisopropylpotassium to sym-diphenylethylene.



Simple organoalkali compounds may be divided very generally into three classes: (1) The colorless monosodium or monopotassium aryls and alkyls, which are insoluble in organic solvents, act as electrolytes when dissolved in zinc alkyls, and are probably heteropolar in the solid state, (2) the more or less intensively colored compounds, in which the carbon atom united with the alkali metal is also in direct union with aromatic rings or a system of multiple bonds and which yield conducting solutions in many organic solvents, and (3) the colorless lithium alkyls, which are soluble in organic solvents, are readily fusible or liquid, sublime or distil unchanged, conduct poorly or not at all in zinc alkyls, and in their physical properties resemble the zinc and cadmium alkyls.

50. Ziegler, German patent, 487,727 (1927); Ziegler and Bahr, Ber., 61, 253 (1928).

Addition has been observed only to unsaturated carbon atoms directly linked or conjugated with a benzene ring or other unsaturated system. The presence of as many as three phenyl groups tends to hinder the reaction.

With respect to the ability of the aforementioned three classes of compounds to add to double bonds, the following characteristics are shown. The evidence indicates that members of class (1) would readily yield addition products. The tendency of the members of class (2) to add is largely determined by the number of aromatic nuclei and unsaturated groups attached to the carbon atom in union with the alkali metal. Only compounds having but one such group in the position defined are capable of smooth addition.

The lithium alkyls comprising class (3) add smoothly but more slowly, the rate changing with the nature of the alkyl radical and apparently alternating as the number of carbon atoms is regularly increased.

Ziegler and co-workers¹⁹ investigated the addition of phenylisopropylpotassium to unsaturated hydrocarbons and obtained the results given in the following table.

TABLE V

The Addition of Phenylisopropylpotassium to Unsaturated Hydrocarbons

<u>Compound</u>	<u>Product (R C₆H₅C(CH₃)₂-)</u>
C ₆ H ₅ CH=CH ₂	C ₆ H ₅ CH(K)CH ₂ R
C ₆ H ₅ CH=CHC ₆ H ₅	C ₆ H ₅ CH(K)CHRC ₆ H ₅
(C ₆ H ₅) ₂ C=CH ₂	(C ₆ H ₅) ₂ C(K)CH ₂ R
(C ₆ H ₅) ₂ C=CHC ₆ H ₅	-----
C ₆ H ₅ CH=CHCH ₃	C ₆ H ₅ CH(K)CHRCH ₃
C ₆ H ₅ (CH ₃)C=CH ₂	C ₆ H ₅ (CH ₃)C(K)CH ₂ R
C ₆ H ₅ CH=CHCH ₂ CH ₂ C ₆ H ₅	C ₆ H ₅ CH(K)CHRCH ₂ CH ₂ C ₆ H ₅
C ₆ H ₅ CH=CHCH=CHC ₆ H ₅	(?)

Benzyl lithium reacts with butadiene in ether to yield, subsequent to hydrolysis and hydrogenation, hydrocarbons like phenylnonane and phenyltridecane.⁵¹

13. Migration of the metal from the nucleus to the side chain.

The first mention of a possible migration of an alkali atom from the nucleus to the side chain of an aromatic compound may be found in the work of Bachmann and Clarke.⁵²

In allowing di-*p*-tolylmercury to react with sodium in

51. Ziegler, Dersch and Wollthan, Ann., 511, 13 (1934).

52. Bachmann and Clarke, J. Am. Chem. Soc., 49, 2089 (1927).

benzene suspension they found that the reaction mixture contained, subsequent to carbonation, benzoic acid (34%), p-toluic acid (30%) and phenylacetic acid (0.36%). The formation of the phenylacetic acid establishes a migration of sodium from the nucleus to the methyl group and is an interesting variation of the lateral metalation of toluene by ethylsodium first observed by Schorigin.²⁰ However, it is uncertain in the Bachmann-Clarke experiment whether migration took place directly or first involved the metalation of benzene, used as a medium, inasmuch as phenylsodium must have formed because of the high yield of benzoic acid. That the migration will occur in the absence of benzene is shown in the latter part of this thesis. In the work of Bachmann and Clarke is witnessed an apparently anomalous reaction since the tolyl radical is more electro-negative than the phenyl radical, according to the work of Kharasch.⁵³ To effect the migration, however, the reaction was allowed to proceed for a month which is a period of time quite different from that most frequently employed in metalation reactions.

Ziegler⁵⁴ prepared p-tolylsodium from p-chlorotoluene and found that by omitting strong heating a migration of the metal from the nucleus to the side chain did not occur. Why Ziegler mentioned the fact that strong heating was

53. Kharasch and Flenner, ibid., 54, 674 (1932).

54. Ziegler, Angew. Chem., 49, 455 (1936).

omitted is not clear since no migration studies had been previously reported.

Morton and co-workers⁵⁵ prepared several acids by the treatment of various halides, dissolved in benzene, with metallic sodium in the presence of carbon dioxide under pressure. It is interesting to note that no migration of the sodium atom was observed in any of the compounds in which this was possible. It is most probable that the carbon dioxide carbonated the nuclear compound before the migration had time to take place. The following table shows their interesting results.

TABLE VI

Preparation of Acids from Organosodium Compounds

<u>Chloride used</u>	<u>Acid isolated</u>	<u>Yield (%)</u>
Chlorobenzene	Benzoic	0-78
<u>m</u> -Chlorotoluene	<u>m</u> -Toluic	5-88
<u>p</u> -Chlorobiphenyl	<u>p</u> -Phenylbenzoic	65-67
<u>p</u> -Chlorotoluene	<u>p</u> -Toluic	95
<u>o</u> -Chlorobenzaldehyde	Phthalaldehyde	47
α -Chloronaphthalene	α -Naphthoic	0
<u>o</u> -Chlorobiphenyl	<u>o</u> -Phenylbenzoic	0
Chlorocyclohexane	Cyclohexanecarboxylic	0
Benzyl Chloride	Phenylacetic	0

55. Morton, Lefevre and Hechenbleikner, J. Am. Chem. Soc., 58, 754 (1936).

A complete discussion on the preparation of lateral compounds as a consequence of migration is included in a later part of this thesis.

14. Lateral organoalkali compounds containing a hetero element.

A few lateral organoalkali compounds, containing a hetero-element, are known and will be discussed briefly.

Phenylacetonitrile is a compound containing a methylene group in which the hydrogens are extremely reactive. In fact, the reactivity of this compound is so great that its ether solution reacts with either sodium or sodium amide forming the metalation product $C_6H_5CH(Na)CN$.⁵⁶ The resulting alkali compound on treatment with alkyl halides forms compounds having the general formula C_6H_5CHRCN . These substances, like the parent nitrile, also react with alkyl halides after metalation to produce compounds having the general formula $C_6H_5CRR'CN$.⁵⁶ⁿ

The above reactions as well as those with esters support the organometallic structure assigned.³ However,

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56. (a) Bodroux and Taboury, Compt. rend., 150, 531, 1274 (1910); (b) Bodroux, ibid., 151, 234, 1357 (1910); (c) Bodroux, Bull. soc. chim., [4], 9, 651 (1911); (d) Upson, Maxwell and Parmelee, J. Am. Chem. Soc., 52, 1971 (1930); (e) Rising and Braun, ibid., 52, 1069 (1930); (f) Rising and Lowe, ibid., 52, 2524 (1930); (g) Rising, Muskat and Lowe, ibid., 51, 262 (1929); (h) Rising and Zee, ibid., 49, 541 (1927); (i) Rising and Zee, ibid., 50, 1699 (1928); (j) Bodroux, Compt. rend., 152, 1594 (1911); (k) Bodroux, Bull. soc. chim., [4], 9, 726, 758 (1911); (l) Bodroux, Compt. rend., 153, 350 (1911); (m) Bodroux and Taboury, Bull. soc. chim., [4], 7, 735 (1910); (n) Bodroux and Taboury, Compt. rend., 150, 1241 (1910).

some reactions indicate that the compound formed has a "nitride" structure, ^{56d} $C_6H_5CH=C=N-Na$, and certain studies indicate that a tautomeric equilibrium mixture of both forms is in best accord with the evidence. ^{56e} and ^f

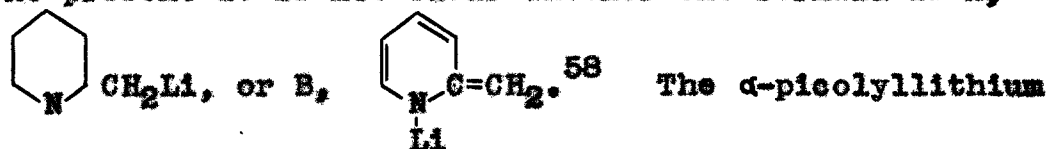
It seems very probable that the isomerism is in the organic ion, $\left[\underset{\text{H}}{\text{C}_6\text{H}_5:\ddot{\text{C}}::\ddot{\text{C}}::\ddot{\text{N}}} \right]^-$ or $\left[\underset{\text{H}}{\text{C}_6\text{H}_5:\ddot{\text{C}}::\ddot{\text{C}}::\ddot{\text{N}}} \right]^-$,
 "Nitride" "Carbide"

and the suggestion has been made ^{56d} that the substance exists only in the nitride form, the condensation reactions at the carbon atom involving rearrangement of the anion during the reaction. However, the distinction between pre-existing tautomerism and rearrangement which occurs during reactions is a fine one which appears to lie beyond the scope of the existing experimental evidence. ²⁹

α -Picolyllithium has been prepared from α -picoline and phenyllithium. When methyllithium was used, the lateral metalation was accompanied by the evolution of methane. ⁵⁷



At present it is not clear whether the formula is A,



57. Ziegler and Zeiser, *Ann.*, 485, 174 (1931).

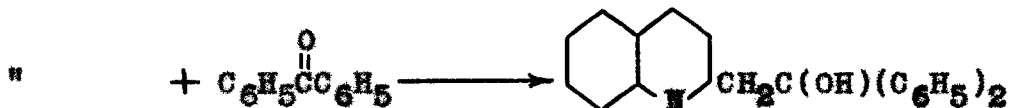
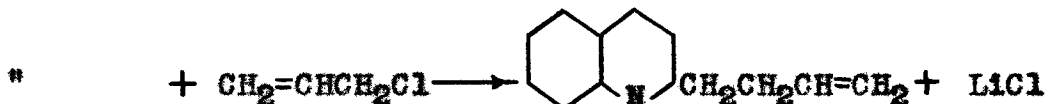
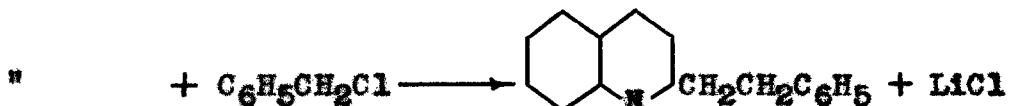
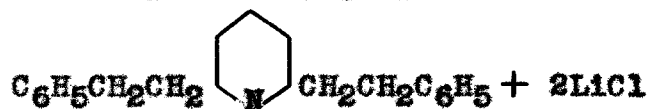
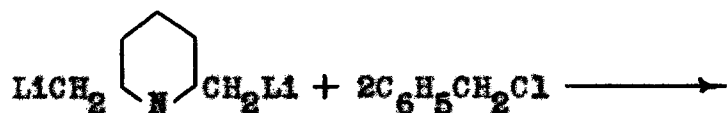
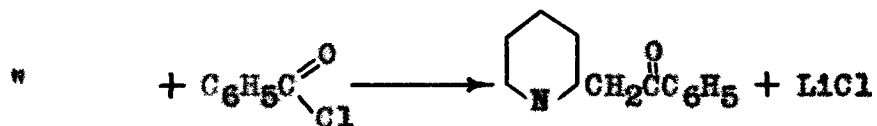
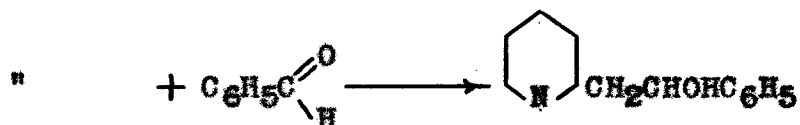
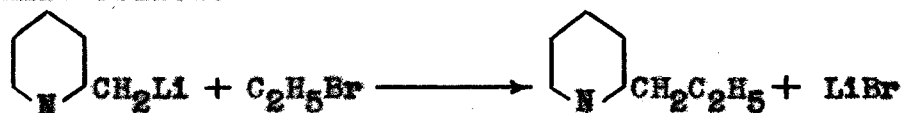
58. Bergmann and Rosenthal, *J. prakt. Chem.*, 135, 267 (1932).

reacts with benzoyl chloride to form α -phenacylpyridine and with benzaldehyde to give phenylpyridomethylcarbinol. It is possible to postulate this substance by a rearrangement of the enolate form, but it is seldom that a carbinol is obtained by this type of condensation, a corresponding benzal derivative usually being the result.⁵⁹ Further proof for formula A is the fact that with benzophenone the α -picolylithium reacts normally while enolates react abnormally with aromatic ketones.⁵⁷ Another indication favorable to formula A is that the compound is colored a reddish-yellow as are the benzyl types while form B would hardly be colored. Bergmann and Rosenthal⁵⁸ further believe that if form B was the correct one, only a mono-lithium compound could be formed by metalation of 2,6-dimethylpyridine or 2,6-lutidine, which would give 2-methyl-6, β -phenethylpyridine upon treatment with benzyl chloride. However, 2,6-lutidine gives a dilithium derivative since 2,6-di- β -phenethylpyridine is obtained upon treatment with benzyl chloride and this is very strong evidence for form A. Even when one mole of phenyllithium and one mole of 2,6-lutidine are reacted the di- and not the mono-lithium compound is formed.

59. Riedel and Straube, Ann., 367, 40 (1909); Braun, Monatsh., 17, 210 (1896); Müller, Ann., 491, 251 (1931).

Quinaldylithium is prepared in a similar manner from quinaldine and phenyllithium using somewhat drastic conditions as no solvent is employed.⁵⁷

A few reactions of heterocyclic lateral organolithium compounds follow.^{57,58}



d-Picolylsodium was also prepared⁶⁰ by the action of sodium amide on d-picoline in the absence of any solvent. Several days were required for this reaction to go to completion.

Gilman and Webb⁶¹ found that metalation of methyl phenyl sulfide proceeded quite unlike that of the related anisole, and, instead of giving an ortho nuclear metalation product, yielded exclusively a lateral metalation.



B. Reactions of Lateral Organosulfide Compounds

The lateral organosulfide compounds undergo reactions which are characteristic of the reactive organometallic compounds. A few exceptions occur and these are amplified in order to distinguish them from the common reactions of organosulfide compounds.

1. Reactions with active hydrogen.

All the organosulfide compounds are decomposed by water, acids, alcohols, etc., with the formation of the parent hydrocarbon. Liquid ammonia decomposes organosulfide compounds rapidly except for the trityl types such as

60. Chichibabin, Rec. trav. chim., 57, 588 (1938).
61. Gilman and Webb, J. Am. Chem. Soc., 62, 987 (1940).

triphenylmethylsodium and -potassium; however, even these are decomposed into triphenylmethane by gaseous ammonia at room temperature. ^{51a, 47b} Except for the hydrolysis reactions of von Grosse, ⁹ no extensive studies on the reactions of trityllithium, -rubidium and -cesium have been made.

2. Reactions with formaldehyde.

Reactions with formaldehyde usually yield a primary alcohol. In the case of benzylolithium, ⁶² like benzylmagnesium chloride, ⁶³ an allylic rearrangement occurs to form g-tolylcarbinol instead of the expected β -phenylethyl alcohol. Triphenylmethylsodium reacts with formaldehyde in a normal manner to give $\beta_2\beta_2\beta$ -triphenylethyl alcohol. ^{51a, 32} Although the triphenylmethylsodium contains an allylic system, it does not undergo a rearrangement with formaldehyde.

3. Reactions with carbon dioxide.

Carbonation is the most frequently employed method for the characterization of metallation products because the acid formed by this reaction is, in general, readily isolated, purified and identified. Gilman and Van Ess ⁶⁴

-
62. Gilman and Brewer, ibid., 56, 1127 (1934).
63. (a) Tiffeneau and Delange, Compt. rend., 137, 573 (1905);
(b) Gilman and Kirby, J. Am. Chem. Soc., 54, 345 (1932);
(c) Austin and Johnson, ibid., 54, 647 (1932).
64. Gilman and Van Ess, ibid., 55, 1258 (1933).

have shown that the yield of acid is greatly increased when carbonation is effected with solid carbon dioxide or by the spray procedure.⁶⁵ Carbonation of phenyllithium with gaseous carbon dioxide gave only a small yield of benzoic acid and such a large quantity of benzophenone that this method was suggested as a means of preparing ketones.

Schlenk and Holtz³⁸ treated benzylsodium obtained from dibenzylmercury with carbon dioxide and obtained phenylacetic acid. Dr. J. E. Kirby⁶⁶ found that after dissolving his benzylsodium in ether, as Schlenk and Holtz did in order to effect an analysis, he was unable to isolate any phenylacetic acid after carbonation. Apparently most of the benzylsodium was destroyed by the ether and the small amount that remained was enough to give the solution a deep brick-red coloration.

Triphenylmethylsodium gives good yields of triphenylacetic acid on carbonation.

The effect of changing the rate of carbonation and the kind of product produced will be considered in the discussion of the experimental work.

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65. (a) Bodroux, Bull. soc. chim., [3], 31, 24 (1904);
(b) Spencer and Stokes, J. Chem. Soc., 93, 70 (1908);
(c) Gilman and Parker, J. Am. Chem. Soc., 46, 2316
(1924); (d) Gilman and Harris, Rec. trav. chim., 50,
1052 (1931).
66. Kirby, J. E., Unpublished thesis, Iowa State Coll.,
(1929).

4. Reaction with carbon monoxide.

Schlenk and Marcus^{31a} failed to obtain a reaction when they treated triphenylmethylsodium with carbon monoxide.

5. Reactions with carbonyl compounds.

The reactions of the carbonyl group with sodium compounds follow closely the pattern of the Grignard reagent. Benzaldehyde and furfural react with triphenylmethylsodium to give phenyltriphenylmethylcarbinol and furyltriphenylmethylcarbinol, respectively. It is interesting to note that triphenylmethylsodium ceases to react with esters and ethyl chlorocarbonate at an earlier stage than do the Grignard reagents to give the corresponding ketone and ethyl triphenylacetate.^{31a,32,67} This fact is suggestive of the abnormal behavior of highly branched aliphatic compounds.⁶⁸

6. Reactions with enolic compounds.

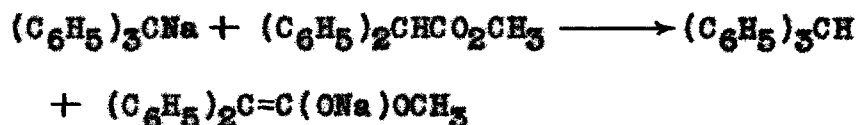
Compounds which are able to form enols (acetone, acetoacetic ester, etc.,) react as the pure enol and simply exchange a sodium atom for the hydrogen atom. For this reason Schlenk and co-workers⁶⁹ have employed triphenylmethylsodium in the preparation and study of crystalline

67. Blum-Bergmann, Ann., 484, 26 (1930).

68. Conant and Blatt, J. Am. Chem. Soc., 51, 1227 (1929).

69. Schlenk, Hillemann and Rodloff, Ann., 487, 135 (1931).

enolates.

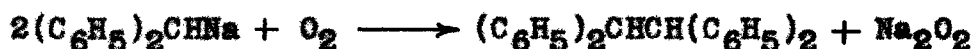


7. Reactions with oxygen.

Müller and Töpel^{70a} in their extensive studies on the oxidation of organometallic compounds passed oxygen gas into an ether solution of benzyl lithium and obtained benzyl alcohol (28%) and bibenzyl (14%). Schlenk,³⁸ on the other hand, obtained a large amount of stilbene on slowly oxidizing benzylsodium.

In some studies on the oxidation of phenyllithium Pacevitz and Gilman^{70b} found that this compound when oxidized with dry air gave phenol (26%), biphenyl (25%) and a very small amount of *p*-phenylphenol.

Oxidation of diphenylmethylnsodium takes place smoothly when a stream of dry air is passed through a liquid ammonia solution of the organoalkali compound⁷¹ and leads to the formation of a hydrocarbon.



Several investigators have reported^{31a,72a} that triphenylsodium reacts with oxygen to give the corresponding

70. (a) Müller and Töpel, Ber., 72, 273 (1939); (b) Pacevitz and Gilman, J. Am. Chem. Soc., 61, 1603 (1939).

71. Wooster, Unpublished observations.

72. (a) Schmid and Falke, Monatsh., 60, 295 (1932); (b) Bachmann and Cockerill, J. Am. Chem. Soc., 55, 2932 (1933).

free radical and subsequently triphenylmethyl peroxide. However, the fact that triphenylmethylmagnesium bromide reacted ^{72b} with air to give triphenylcarbinol (in the form of its bromo-magnesium salt) as the chief product led Bachmann and Wiselogle ^{31b} to investigate the behavior of the sodium derivative. Here, too, they found that by passing air through a solution of triphenylmethylsodium, triphenylcarbinol was the principal product with only a small amount of triphenylmethylperoxide being formed.

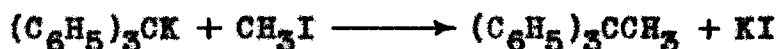
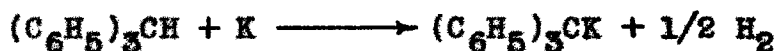


This fact suggests that the formation of an organic peroxide as an oxidation product is typical only of those organo-alkali compounds which are derivatives of free radicals. ⁷¹

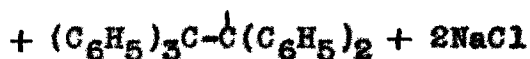
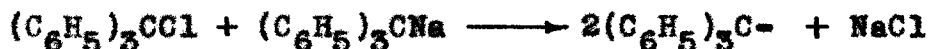
8. Reactions with organic halides.

Except for the triarylmethylalkali compounds the reactions with organic halides have not been studied to any great degree. Benzylsodium reacts with benzyl halides to form dibenzyl. ^{4b} Generally, the organic halides react smoothly with the triphenylmethylalkalis, ^{31a} and the extensively studied triphenylmethylsodium has been shown to react readily with methyl iodide, bromobenzene and benzyl chloride, in liquid ammonia, to give 1,1,1-triphenylethane,

tetraphenylmethane and 1,1,1,2-tetraphenylethane, respectively.^{4b,7} The procedure followed in preparing the first of these three hydrocarbons was to treat triphenylmethane with potassium in liquid ammonia and then add the methyl iodide.



In certain instances the action of organic halides on triphenylmethylsodium results in the formation of free radicals as in the cases of triphenylchloromethane^{31a,7} and diphenyldichloromethane.⁷³



9. Reactions with mercury and mercuric chloride.

Mercury and mercuric chloride react with the lateral organoalkali compounds to give the mercurial in most cases. Benzylsodium and benzyl lithium react with mercuric chloride to give dibenzylmercury in a very short time. Mercury was found to react with benzyl lithium at a much slower rate, dibenzylmercury being isolated after a reaction period of fifteen hours. Diphenylmethylsodium when treated with

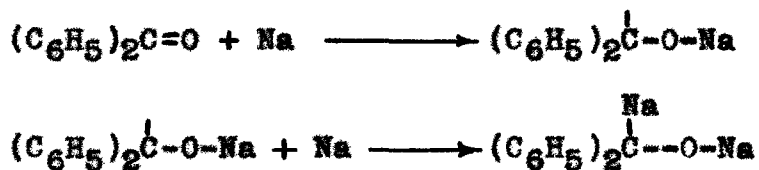
73. Schlenk and Mark, Ber., 55, 2285, 2299 (1922).

mercuric chloride failed to produce any mercurial but sym-tetraphenylethane was isolated.⁷⁴



10. The metal ketyls.

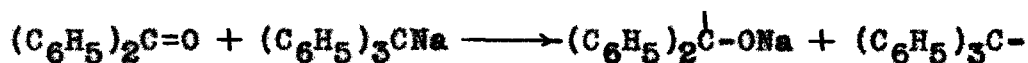
The opening of the double bond of the carbonyl group by means of alkali metals may be found in the earliest work of Schlenk and his co-workers.^{47a,14} It was during these researches that they discovered the metal ketyls, or compounds containing a trivalent carbon atom and having the general formula, $\text{R}_2-\overset{\text{I}}{\text{C}}-\text{O}-\text{metal}$. These compounds are able, like the free radicals, to further add another atom of alkali metal, to form di-alkalimetal ketyls. For example, benzophenone adds two atoms of sodium. First, in the course of the reaction there arises a deep blue solution of the "metal ketyl" and then, after several hours, it changes to the red-violet color of the lateral organo-alkali compound according to the following equations:



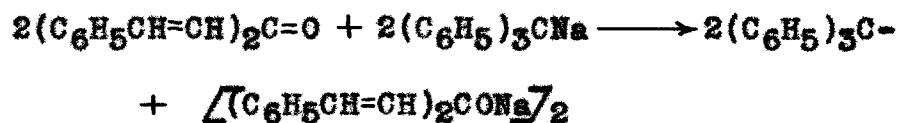
74. Ziegler, Ber., 64, 447 (1931).

These reactions may also be carried out in liquid ammonia⁷⁵ in which the three participating compounds are soluble.

Apparently the only lateral organoalkali compound used in the study of the ketyls is triphenylmethylsodium. In a reaction with this organoalkali compound, benzophenone was partly converted into the "metal ketyl".³²



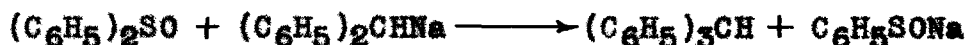
Dibenzalacetone may be converted into a pinacolate³ as follows:



The pinacol formed upon hydrolysis of this product passes spontaneously into a pinacolone.

11. Reaction with sulfur compounds.

With sulfur dioxide, triphenylmethylsodium forms triphenylmethylsulfinic acid, $(\text{C}_6\text{H}_5)_3\text{CSO}_2\text{H}$. Diphenylsulfoxide⁷⁶ reacts with the closely related diphenylmethylsodium according to the following reaction:



The sodium benzenesulfenate is a violet powder which is transformed into the colorless salt, sodium benzenesul-

75. (a) Schlubach, *Ber.*, 48, 12 (1915); (b) Wooster, *J. Am. Chem. Soc.*, 50, 1388 (1928).

76. Schönberg and Stephenson, *Ber.*, 66, 250 (1933); Bergmann, *ibid.*, 65, 457 (1932).

finite, by the absorption of one-half mole of oxygen.

12. Reaction with nitrogen oxides.

Schlenk and Bergmann^{47b} reacted the tritylalkalis with some oxides of nitrogen and obtained well defined products having an unproved structure.

13. The cleavage of diethyl ether.

The great difference in reactivity between the members of the benzylalkali series is strikingly illustrated by the rate at which they cleave diethyl ether. Benzyl lithium does not decompose diethyl ether^{20,36} appreciably, even when in contact with this solvent for extended periods of time, while benzyl sodium destroys the ether in a few minutes.³⁸

14. The color test.

The color test⁷⁷ with Michler's ketone is generally very reliable with organoalkali compounds, although a very surprising result was obtained by Young⁷⁸ in which triphenylmethyl lithium gave a very good color test while the corresponding sodium and potassium compounds did not give this test. This result was attributed to the formation of

77. Gilman and Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

78. Young, R. V., Unpublished thesis, Iowa State Coll., (1936).

metal ketyls by these compounds. However, it is interesting to note that benzophenone reacted with benzylpotassium to give good yields of diphenylbenzylcarbinol.¹⁸

15. Lateral organoalkali compounds as metalating agents.

The use of lateral organoalkali compounds as metalating agents has not been investigated very thoroughly for obvious reasons. Furan, a nucleus to which pronounced aromaticity has been attributed by various workers, was found to give high yields of metalation product when treated with phenyllithium in ether solution.^{28,79} The reactants were heated at reflux for twenty hours and then carbonated with powdered dry ice, giving a 40% yield of d-furoic acid. Other workers²⁴ investigating the use of organosodium compounds in the metalation of furan found benzylsodium to be an exceedingly good metalating agent inasmuch as a 58% yield of d-furoic acid was obtained.

Dr. T. H. Cook⁸⁰ obtained a 78% yield of 4-carboxydibenzofuran when benzylsodium was allowed to react with dibenzofuran in toluene solution.

16. Reactions of the organoalkali compounds obtained by normal and dimerizing additions of alkali metal to ethylenic linkages.

Schlenk and Bergmann^{47b} have shown that the products

79. Boatner, Charlotte, Unpublished results.

80. Cook, T. H., Unpublished thesis, Iowa State Coll. (1940).

obtained in the normal and dimerizing additions of sodium metal to an ethylenic bond react differently with a common reagent. Table VII indicates the products obtained in each case.

TABLE VII

Reactions of the Organoalkali Compounds Obtained by Normal and Dimerizing Additions of Alkali Metal to Ethylenic Linkages

<u>Reagent</u>	<u>Product of the reaction with</u>	
	<u>(Representing the normal addition)</u>	<u>(Representing the dimerizing addition)</u>
	$\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2 \\ \quad \\ \text{Na} \quad \text{Na} \end{array}$	$\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C}-\text{CH}_2\text{CH}_2-\text{C}(\text{C}_6\text{H}_5)_2 \\ \quad \quad \quad \\ \text{Na} \quad \quad \quad \text{Na} \end{array}$
	(Representing the normal addition)	(Representing the dimerizing addition)
2CH ₃ I	$\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2 \\ + \text{C}_2\text{H}_6 + 2\text{NaI} \end{array}$	$\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ \quad \quad \\ (\text{C}_6\text{H}_5)_2\text{C}-\text{CH}_2\text{CH}_2-\text{C}(\text{C}_6\text{H}_5)_2 \\ + 2\text{NaI} \end{array}$
2C ₆ H ₅ CHO (+ H ₂ O)	$\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2, \\ \text{sodium benzoate} \\ \text{and benzyl al-} \\ \text{cohol} \end{array}$	$\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C}-\text{CH}_2\text{CH}_2-\text{C}(\text{C}_6\text{H}_5)_2 \\ \quad \quad \\ \text{C}_6\text{H}_5\text{CH} \quad \text{C}_6\text{H}_5\text{CH} \\ \quad \quad \\ \text{ONa} \quad \quad \text{ONa} \end{array}$
2C ₂ H ₅ N=C=S	$\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2 \\ + \text{C}_2\text{H}_5-\text{N}-\text{C}-\text{C}-\text{N}-\text{C}_2\text{H}_5 \\ \quad \quad \quad \\ \text{NaS} \quad \text{S} \quad \text{Na} \end{array}$	$\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C}-\text{CH}_2\text{CH}_2-\text{C}(\text{C}_6\text{H}_5)_2 \\ \quad \quad \quad \\ \text{C}_2\text{H}_5-\text{N}-\text{C}=\text{S} \quad \quad \text{S}=\text{C}-\text{N}-\text{C}_2\text{H}_5 \\ \quad \quad \quad \\ \text{Na} \quad \quad \quad \text{Na} \end{array}$
2C ₆ H ₅ Br	$\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2 \\ + \text{C}_6\text{H}_5-\text{C}_6\text{H}_5 + 2\text{NaBr} \end{array}$	
CO	No reaction	
NO	$\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2 \\ + \text{Na}_2\text{N}_2\text{O}_2 \end{array}$	

17. Relative reactivities of lateral organoalkali compounds.

Table VIII summarizes some interesting results obtained in the relative reactivity studies on the phenylethyne-alkali compounds by Gilman and Young.² It may be clearly seen that the lithium compound reacts to an extent which is more closely related to the Grignard reagent than to the other organoalkali compounds. This is not extremely surprising in view of the fact that there are other reactions in which the lithium compounds act like the Grignard reagents.⁶²

TABLE VIII

Time (in Hours) Required for Reaction of $C_6H_5C\equiv CM$ with

Benzonitrile

(1) $C_6H_5C\equiv CMgBr$	87, 85
(2) $C_6H_5C\equiv ClLi$	57, 63
(3) $C_6H_5C\equiv CNa$	6.5, 7.0
(4) $C_6H_5C\equiv CK$	4.3, 4.5
(5) $C_6H_5C\equiv CK$	5.3, 5.1
(6) $C_6H_5C\equiv CRb$	4.8, 4.9
(7) $C_6H_5C\equiv C Cs$	3.8, 3.9

The last three runs were at a lower concentration than the first four, the run with phenylethynepotassium being

repeated to give a more exact comparison. The color test⁷⁷ was used as a criterion of completion of reaction.

Much mention has been made of the triphenylmethyl-alkalis with only little regard paid to other triarylmethyl-alkali compounds. The reactions in almost all cases are similar. Physically, however, there is a definite variation in their color as may be seen from Table IX.

TABLE IX

Color of Triarylmethylsodium Compounds^{31a}

<u>Substance</u>	<u>Color</u>
Triphenylmethylsodium	Red
Biphenylene- <i>p</i> -anisylmethylsodium	Red
Biphenylenephénylmethylsodium	Orange-red
Dibiphenyl- α -naphthylmethylsodium	Dark violet
Phenyl- α -naphthylbiphenylmethylsodium	Blue-violet
Tribiphenylmethylsodium	Blue

III. EXPERIMENTAL

The apparatus used in many of the following experiments is described below and will be referred to as the "usual apparatus". Also, the term "usual apparatus" will be followed by a number in parentheses which will designate the capacity of the flask used in the experiment, i.e., "Into the usual apparatus (500 cc.) was placed, etc.."

A round-bottomed Pyrex flask of the three-necked variety was equipped in the usual manner with a Hopkins condenser having a nitrogen inlet, mercury-sealed stirrer operated by an electric motor, and thermometer. After setting up the dry apparatus, dry nitrogen gas was allowed to sweep through for one hour.

All glassware used in the following experiments was first washed in the acid bath and then in sequence with tap water, ammonium hydroxide, tap water, distilled water and finally dried for several hours in the drying oven.

Ordinary rubber stoppers were found to serve the experimental purposes very well, although they did deteriorate with use. The protective sulfur-talcum coating was always removed by boiling the stoppers in sodium hydroxide solution prior to use.

At any time when it was necessary to reflux the reaction mixture, the stoppers were wired to the flask in order to prevent them from "popping" out because of the swelling caused by the hot solvent. This was observed very rigorously in order to prevent potentially hazardous accidents. Duprene stoppers are more resistant to the deteriorating effects of boiling solvents and are superior to the ordinary rubber stoppers.

As a general rule the pyrogallol solution in the nitrogen purification train was changed every two or three weeks depending upon the extent of its usage.

A. Sodium Compounds

1. An improved method for preparing phenylsodium.

Into the usual apparatus (500 cc.) was placed a mixture of 150 cc. of toluene, 11.5 g. (0.5 g. atom) of sodium sand, and 22.5 g. (0.2 mole) of chlorobenzene. After standing at room temperature for about forty-five minutes, the temperature began to rise and by appropriate cooling was not allowed to exceed 40° during the entire reaction period which lasted about two hours. When the temperature started to fall, the mixture was immediately poured jet-wise on crushed solid carbon dioxide. After all the carbon dioxide

had disappeared the excess sodium sand was carefully destroyed by the cautious drop-wise addition of distilled water, enough water being added to equal one-third the volume of toluene. The layers were separated and the toluene was washed twice with water, the washings being added to the original alkaline layer. The combined alkaline layers were washed once with ether and any dissolved ether removed by heating on the hot-plate. The brownish solution was cooled and acidified with dilute hydrochloric acid which caused the benzoic acid to precipitate as a slightly yellow solid. This was filtered and crystallized once from hot water. The yield of benzoic acid (mixed melting point) was 21.2 g. or 87% of the theoretical.¹⁸

2. A new method for preparing benzylsodium.

The preliminary operations in the following experiment were similar to those described in the "Improved Method for Preparing Phenylsodium". After the formation of phenylsodium the suspension was refluxed for three hours. As soon as refluxing started, the black suspension began to take on a brick-red color, and at the end of three hours the color was typical of benzylsodium. Carbonation was effected in the usual manner by pouring on solid carbon dioxide. The sodium was destroyed in the usual manner

and the alkaline layer was treated as before. Acidification of the cooled solution produced an oil which solidified on cooling. The solution was filtered and the mother liquor extracted with ether in order to insure recovery of all benzoic, phenylacetic, malonic and toluic acids which may have formed. After repeated crystallizations from water and treatment of the dried solid with chloroform, only phenylacetic acid, melting point 76-76.5°, (mixed melting point, also) was obtained. The yield was 20.9 g. or 77%.¹⁸

Table X gives a complete summary of the experimental conditions tested in order to perfect this preparation.

TABLE X

Effect of Prolonged Refluxing on the Metalation of Toluene with Phenylsodium

Run	Reflux period (Hours)	Phenylacetic acid <u>G.</u>	Phenylacetic acid <u>%</u>	Benzoic acid <u>G.</u>	Benzoic acid <u>%</u>
1	0	0	0	21.2	87
2	1	16.9	62	1.6 (Very crude)	6.6
3	3	20.9	77	0	0
4	6	21.6	79.4	0	0
5	20	18	66	0	0

From the results obtained it may be seen that the conditions of run three are most ideal as far as practicability is concerned.

3. An attempt to metalate toluene with phenylsodium in benzene solution.

The phenylsodium used in this experiment was prepared in accordance with the method of Ziegler.⁵⁴ Into the usual apparatus (500 cc.) was placed a mixture of 200 cc. of dried, thiophene-free benzene, 11.5 g. (0.5 g. atom) of sodium sand and 22.5 g. (0.2 mole) of K_2CO_3 -dried chlorobenzene. After starting, the reaction mixture was allowed to stir for sixteen hours, the temperature at no time rising above 40° . At the end of this time 18.5 g. (0.2 mole) of toluene was added and allowed to stir for forty-eight hours at room temperature. The color of the reaction mixture became a dark green. Carbonation and extraction of the crude acidic material was accomplished in the usual manner. Crystallizing once from hot water gave 17.8 g. (72.4%) of crude benzoic acid melting at $115-118^\circ$.

In order to eliminate the possibility of any of the toluic acids being present, as an impurity, and to indicate that phenylacetic acid was the only impurity, a sample of the crude acidic material was oxidized as follows. Six grams of the mixture was refluxed for three hours in a solution of 14.9 g. of sodium dichromate, 20 cc. of concentrated sulfuric acid and 30 cc. of water. Some oxidation occurred as was evidenced by the formation of the green chromic ion. The reaction mixture was poured into cold

water, filtered, boiled with dilute sulfuric acid, filtered, dissolved in dilute sodium hydroxide, precipitated by dilute sulfuric acid, filtered, washed and dried. The melting point without further recrystallization was 120.5-121° indicating the absence of dibasic acids. Malonic acid was shown to be absent by the complete solubility of the original material in chloroform. The recovery of the purified benzoic acid was 5.4 g. or 90% of the starting material.

4. An attempt to prepare benzylsodium from benzyl chloride and sodium.

A mixture of 150 cc. of toluene and 18.4 g. (0.8 g. atom) of sodium sand was placed into the usual apparatus (500 cc.). To this was added fifteen drops of dry benzyl chloride and the mixture was allowed to stir at 26°. The sodium metal lost its brilliance and assumed a pink color. No perceptible rise in temperature occurred after adding a total of 25.4 g. (0.2 mole) of benzyl chloride. The reaction mixture gave no color test after being stirred for twenty-four hours at room temperature. The color test was still negative after allowing the reaction to stand at room temperature for six weeks. Benzyl bromide gave the same negative results.

5. An attempt to metalate benzene with benzylsodium.

A 0.2 mole run of benzylsodium was made by the usual procedure. The toluene was then removed by carefully

distilling, in a rapid stream of dry nitrogen, over an electric hot-plate. Care was taken not to allow the bottom of the flask to get much hotter than the distilling temperature. To the dry residue was added 150 cc. of carefully dried benzene and the mixture allowed to stir at room temperature for fourteen hours. After carbonation and repeated fractional crystallizations from hot water there was no indication of benzoic acid being present. The yield of phenylacetic acid, melting point $76.5-77^{\circ}$, was 15.3 g. or 56%.

6. Preparation of p-tolylsodium.

In each of the experiments, the results of which are given in Table XI, 12.7 g. (0.1 mole) of p-chlorotoluene, 5.5 g. (0.23 g. atom) of sodium sand and 75 cc. of solvent were used. The use of finely divided sodium makes the reaction start more promptly and also run a smoother course. It is recommended that the fine sodium be freshly prepared for each experiment. Reaction, as a rule, began immediately when the p-chlorotoluene was added to the sodium in the organic medium, being accompanied by an immediate rise in temperature and the formation of black specks on the sodium. The mixture was stirred rapidly and the temperature kept between $35-40^{\circ}$. After about one and one-half hours the

temperature showed no further tendency to rise, the cooling bath was removed, and stirring was continued until room temperature was again reached. In carbonating with solid carbon dioxide, it was desirable to add 100-200 cc. of dry ether to the carbon dioxide, when benzene was used as the medium, in order to eliminate freezing. Excess sodium was removed as before and the *p*-toluic acid crystallized from hot water after being filtered from the acidified solution.¹⁸

TABLE XI

Preparation of *p*-Tolylsodium in Various Solvents

0.1 Mole of *p*-Chlorotoluene

<u>Solvent</u>	<u><i>p</i>-Toluic Acid</u>	
	<u>G.</u>	<u>Σ</u>
Benzene	8.9	65.5
Benzene	9.5	70.0
Cyclohexane	7.8	57.3
Cyclohexane	7.6	56.0
Pet. Ether (70-80°)	10.1	74.3
Pet. Ether (70-80°)	9.7	71.3
Toluene	10.9	80.1
Toluene	10.8	80.0

7. Migration of sodium in *p*-tolylsodium prepared from *p*-chlorotoluene.

In each of the experiments, the results of which are

given in Table XII, the *p*-tolylsodium was prepared in accordance with directions given above from 0.1 mole of *p*-chlorotoluene, 0.23 g. atom of sodium sand, and 75 cc. of the designated solvent. The yields of the phenylacetic acid are based on the initial 0.1 mole of *p*-chlorotoluene, and not on the per cent of *p*-tolylsodium obtained from the *p*-chlorotoluene.

TABLE XII

Preparation of Benzylsodium by Heating
p-Tolylsodium in Some Solvents

<u>Solvent</u>	<u>Reflux period,</u> <u>(Hours)</u>	<u>Yield of</u> <u>Phenylacetic acid</u>	
		<u>G.</u>	<u>%</u>
Benzene	24	7.1	52.2
Benzene	16	6.8	50.0
Benzene	12	6.6	48.5
Toluene	4	8.5	62.0
Toluene	14	10.75	79.0
Toluene	14	10.7	79.0
Cyclohexane	18	7.3	53.7
Cyclohexane	14	7.9	58.1
Pet. ether (70-80°)	18	8.5	62.5

8. Migration of sodium in *p*-tolylsodium prepared from di-*p*-tolylmercury.

In each of the following experiments, the results of

which are given in Table XIII, the p-tolylsodium was prepared by placing into the designated quantity of solvent 7.7 g. (.02 mole) of di-p-tolylmercury and 11.5 g. (0.5 g. atom) of sodium wire squeezed directly into the solvent. After completion of stirring and refluxing, the reaction mixtures were carbonated and worked up in the usual manner. The excess sodium did not cause any inconvenience as it remained in the reaction flask in the form of an amalgam.

TABLE XIII

Effect of Solvents on the Preparation of Benzylsodium from Di-p-tolylmercury

Run	Solvent	Reflux Period (Hours)	Phenylacetic Acid		Benzoic Acid	
			G.	%	G.	%
1	Benzene (195 cc.)	19	1.35	24.7	.70	14.3
2	Ligroin (160 cc.)	19	3.1	57	0	0
3	Toluene (160 cc.)	5.5	3.6	66	0	0

Notes on the individual runs:

- Run 1. a) A brown suspension of p-tolylsodium began to form as soon as the ingredients were mixed.
b) The benzoic and phenylacetic acids were separated by fractional crystallization from water.
c) No p-toluic acid could be isolated.

Run 2. a) Reaction did not start until after ten minutes of heating.

b) Di-p-tolylmercury is not very soluble in ligroin but apparently it reacted completely since not even a trace could be recovered.

Run 3. The reaction started immediately.

9. Migration of sodium in m-tolylsodium.

In each of the experiments listed in Table XIV the usual apparatus (200 cc.) containing a mixture of 12.7 g. (0.1 mole) of m-chlorotoluene, 5.7 g. (0.25 g. atom) of sodium sand and 100 cc. of dry, unsaturate-free ligroin was employed. The experimental conditions were changed as indicated with significant observations listed as notes. The usual procedure was used in working up the reaction mixtures.⁸¹

TABLE XIV

Effect of Refluxing upon the Yield of Benzylsodium from m-Tolylsodium

<u>Run</u>	<u>Reflux Period</u>	<u>Phenylacetic Acid</u>	
		<u>G.</u>	<u>%</u>
1	10 mins.	.59	4.5
2	1 hr.	1.13	8.5
3	7.5 hrs.	.72	5.3
4	20 hrs.	.63	4.7

81. Gilman and Pacevitz, J. Am. Chem. Soc., 62, 673 (1940).

Notes on the individual runs:

Run 1. a) The reaction was started by heating the mixture to reflux, then immediately cooling to 35-40° and allowing the reaction to proceed at this temperature, with controlled cooling, for six hours.

b) Only 2 cc. of an oily substance with a strong phenylacetic odor was obtained on acidification of the alkaline layer.

c) The neutral layer yielded nothing but 2.5 g. of a sticky black tar from which no definite compound could be extracted.

Runs 2 and 3. Same as run 1.

Run 4. a) There was no reaction after stirring the mixture at room temperature for two hours. The solution became a clear yellow on heating to a gentle reflux after which it was immediately cooled. Two additional hours of stirring at room temperature were required before a spontaneous temperature rise was noted and then, as in the other runs, the suspension began to turn black.

b) A small aliquot of the reaction mixture was carbonated before refluxing was started. Pure m-toluic acid (mixed melting point) was obtained.

This sharp melting point indicated that p-chlorotoluene from which p-toluic acid would result was absent.

c) Toluene could not be found in any of the runs.

10. Preparation of m-toluic acid.

Into the usual apparatus was placed 5.7 g. (0.25 g. atom) of sodium sand, 12.7 g. (0.1 mole) m-chlorotoluene and 100 cc. of ligroin. The mixture was heated to reflux and then immediately cooled to 30°. The temperature was kept between 35-40° for six hours and then carbonated by pouring on crushed solid carbon dioxide. After acidification of the alkaline layer, 11.5 g. (84.6%) of m-toluic acid, melting point 108-109° (Lit. 110-111°), was obtained. A mixed melting point was used to check the product.

11. An attempt to prepare e-tolylsodium from e-chlorotoluene.

The same quantities of material were employed as in the above preparation. No change occurred on stirring at room temperature. Unlike the m-chlorotoluene there was no color change when the reflux temperature was reached. Refluxing was continued for two and one-half hours, no color test being obtained with Michler's ketone after this period of time.

Upon addition of the o-chlorotoluene to the sodium sand in the ligroin, many little bubbles were seen to rise from the metal. It is most probable that a very rapid reaction occurred between the two substances whereupon the sodium immediately became coated with sodium chloride causing the reaction to stop. All materials were carefully dried.

The small bubbles may have been caused by a localized generation of heat which vaporized some of the ligroin.

12. Preparation of di-m-tolylmercury.⁸²

A solution of 43 g. (0.25 mole) of m-bromotoluene in 100 cc. of ether was added slowly, with stirring, to a mixture of 12 g. (0.5 g. atom) of magnesium in 250 cc. of ether. Stirring was continued for four hours after addition of the halide. To the Grignard reagent was slowly added 34 g. (0.125 mole) of dried mercuric chloride and allowed to stir for twelve hours. The reaction mixture was poured into ice water, hydrolyzed and then treated with 25 cc. of concentrated hydrochloric acid. The layers were separated and the ether layer dried over calcium chloride. The sludge was extracted with 600 cc. of ether which was also dried and combined with the original ether layer. The extracts were filtered and the ether was evaporated.

82. Marvel and Gould, ibid., 44, 153-7 (1922).

The yield of crude mercurial, melting point 90-95°, was 22.6 g.

The crude mercurial was pulverized very thoroughly and then added to a solution of 6 g. of hydrated stannous chloride⁸⁵ in 65 cc. of water to which had been added 15 g. of sodium hydroxide in 65 cc. of water. The suspension was stirred very vigorously for three hours, then filtered, washed thoroughly and allowed to dry. The dried material was extracted overnight with chloroform and then the solvent was evaporated. The yield of pure di-m-tolylmercury, melting point 101-102°, was 12 g. or 52%.

13. Preparation of di-o-tolylmercury.⁸²

The exact procedure was followed as in the preparation of di-m-tolylmercury with the exception that o-bromotoluene was used. The yield of di-o-tolylmercury, melting point 106-107°, was 18 g. or 58%. No attempt was made to obtain the maximum yield of either compound.

14. Migration of sodium in o-tolylsodium prepared from di-o-tolylmercury.

Into the usual apparatus (200 cc.) was placed a mixture of 7.7 g. (0.02 mole) of di-o-tolylmercury, 10 g. (0.45 g. atom) of sodium wire and 160 cc. of dry,

⁸⁵. Maynard, *ibid.*, 54, 2118 (1932).

unsaturate-free ligroin. The reaction started after twenty minutes of refluxing and vigorous stirring. It was then refluxed for eighteen hours, cooled and carbonated. The phenylacetic acid was extracted in the usual manner, no o-toluic acid or phenylmalonic acid being obtained. The yield was 2.02 g. (37.2%). A mixed melting point was used to check the product with authentic phenylacetic acid.¹⁸

15. Migration of sodium in m-tolylsodium prepared from di-m-tolylmercury.

The same quantities of materials and procedure were used as in the preceding experiment. The reaction started after fifteen minutes of refluxing and the yield of phenylacetic acid was 0.95 g. or 17.5%.¹⁸

16. Rapid and slow carbonation of benzylsodium in toluene.

Two parallel preparations of benzylsodium were made in the usual manner from 11.2 g. (0.1 mole) of chlorobenzene, 5.7 g. (0.25 g. atom) of sodium sand and 75 cc. of dried toluene. One of these runs was carbonated by pouring on crushed solid carbon dioxide in such a manner that the addition was completed in five seconds. The other run was slowly carbonated by allowing dried gaseous carbon dioxide to pass over the surface of the stirred solution. The color test was negative after four to five hours.

The reaction mixtures were worked up as follows after the alkaline layer had been obtained in a clear state. The acidified layer was extracted with a total volume of 250 cc. of ligroin, the extracts were then filtered and distilled in order to obtain the greatest bulk of the phenylacetic acid. The aqueous layer was filtered and extracted four times with ether. Since phenylmalonic acid is insoluble in ligroin, soluble in water and very soluble in ether, the ether extract contained all of the phenylmalonic acid and the small amount of phenylacetic acid that may have escaped the ligroin extraction. The ether was distilled and the phenylacetic acid removed from the phenylmalonic acid by washing the solid residue with chloroform in which the phenylmalonic acid is also very insoluble but which is easier to remove than the ligroin. The phenylmalonic acid remained as a white crystalline solid and was filtered from the chloroform solution of the phenylacetic acid. The phenylmalonic acid decomposed sharply at 144-145° with a very vigorous evolution of carbon dioxide and was also checked by the neutral equivalent.

Anal. Calcd. for $C_9H_8O_4$: neut. equiv., 90. Found: neut. equiv., 91, 92.

Table XV gives a comparison of the effect of change in rate of carbonation on the yield of phenylmalonic acid from benzylnaodium.

TABLE XV

Effect of the Rate of Carbonation on the Yield of Phenylmalonic Acid from Benzylsodium

<u>Carbonation Period</u>	<u>Phenylacetic Acid</u>		<u>Phenylmalonic Acid</u>	
	<u>G.</u>	<u>%</u>	<u>G.</u>	<u>%</u>
4-5 hours	2.4	17.6	3.8	42.2
5 seconds	9.9	72.9	0.0	0.0

17. Rapid and slow carbonation of benzylsodium obtained from dibenzylmercury.

Two parallel experiments were performed, each involving a mixture of 7.7 g. (0.02 mole) of dibenzylmercury, 10 g. (0.43 g. atom) of sodium wire and 160 cc. of dried toluene. Each of the mixtures was stirred for forty-five minutes at room temperature with no apparent change. However, the reactions started in fifteen minutes when prompted by a reflux temperature which was subsequently applied for four hours. The reaction mixtures were cooled, carbonated and worked up as in the preceding experiment.¹⁸ Table XVI shows the results.

TABLE XVI

Effect of the Rate of Carbonation on Authentic Benzylsodium Prepared from the Mercurial

<u>Carbonation Period</u>	<u>Phenylacetic Acid</u>		<u>Phenylmalonic Acid</u>	
	<u>G.</u>	<u>%</u>	<u>G.</u>	<u>%</u>
4-5 hours	0.46	8.5	0.81	22.8
5 seconds	3.3	61.0	0.03	<1

18. Rapid and slow carbonations of *n*-amylsodium in ligroin.

Table XVII gives the results obtained in two parallel sets of experiments. Conditions up to the point of carbonation were the same in each set with the exception of time and temperature. The usual apparatus (200 cc.), with the inclusion of a dropping funnel, was used. Into the flask was placed 8.75 g. (0.38 g. atom) of sodium sand in 75 cc. of ligroin and to this was slowly added 16.5 g. (0.155 mole) of *n*-amyl chloride in 15 cc. of ligroin over a period of one hour. At the end of this time the suspension assumed a deep blue color. The reaction mixtures were resolved by the same method as used for the phenylacetic-phenylmalonic acid mixtures.⁸⁴

TABLE XVII

Effect of Varying the Reaction Time and Temperature on the Yield of *n*-Butylmalonic Acid

Run	Carbonation Period	Caproic Acid		<i>n</i> -Butylmalonic Acid	
		G.	%	G.	%
1	5 hours	3.53	19.5	1.83	14.8
2	5-10 seconds	6.52	36.4		<1
1a	5 hours	2.72	15.2	2.10	16.9
2a	5-10 seconds	6.91	38.5	0.18	1.5 (Very oily solid)

84. Gilman and Pacevitz, ibid., 62, 1301 (1940).

Notes on the individual runs:

Runs 1 and 2: The reaction mixture was stirred for one hour at 27-28° and then for two hours at 42° after addition of the n-amyl chloride.

The run on the rapid carbonation was rechecked, the yield of caproic acid being 6.8 g. or 38%.

Runs 1a and 2a: The reaction mixture was stirred for four hours at 27-28° after the addition of the n-amyl chloride.

19. Rapid and slow carbonations of n-amylsodium in low-boiling petroleum ether.

In two parallel experiments using the same quantities of materials as in the preceding experiment, and substituting 28-33° b. p. petroleum ether for the ligroin, the results listed in Table XVIII were obtained. The n-amyl chloride was added over a period of two hours, then 25 cc. more solvent was added and the mixture stirred at 26-28° for four hours. In the rapid carbonation 0.04 g. of acid, melting point 183-184°, was obtained and has not been identified.⁸⁴

TABLE XVIII

Effect of Changing Solvent on the Yield
of n-Butylmalonic Acid

<u>Carbonation</u> <u>Period</u>	<u>Caproic Acid</u>		<u>n-Butylmalonic Acid</u>	
	<u>G.</u>	<u>%</u>	<u>G.</u>	<u>%</u>
5 hours	3.1	17.3	3.9	31.4
5-10 seconds	9.2	51.5	0	0

20. Rapid gaseous carbonation of n-amylsodium.

The n-amylsodium was prepared in the same quantity as before, using ligroin as the reaction medium. The reaction mixture was stirred at 28° for four hours after addition of the n-amyl chloride and carbonation was carried out by passing a very rapid stream of dried gaseous carbon dioxide over the surface of the very vigorously stirred mixture. A negative color test was obtained after four minutes and ten more minutes were allowed for completion of the reaction. The yield of n-caproic acid was 5.3 g. (30%) and of n-butylmalonic acid, 1.2 g. (9.7%).

21. Rapid carbonation of n-amylsodium after allowing it to reach a possible equilibrium with amyldenedisodium.

To a mixture of 26.3 g. (1.15 g. atom) of sodium sand in 150 cc. of ligroin was added a solution of 50 g. (0.47 mole) of n-amyl chloride in 40 cc. of ligroin over a period of two hours. This was allowed to stir at room temperature

for sixty-two hours and then carbonated by rapidly pouring on crushed solid carbon dioxide. The sodium metal was cautiously hydrolyzed and the alkaline layer prepared as before. After acidification and extraction of the n-caproic acid with chloroform the aqueous layer was extracted with ether. This extract, which supposedly was to contain any n-butylmalonic acid, yielded a gummy, cream-colored mass on evaporation. On extraction with cold water, 0.55 g. of a solid acidic material was obtained which, after two crystallizations from hot water, melted sharply at 183-184° and has not been identified. The yield of n-caproic acid was 9.4 g. (20%); a very small amount of impure n-butylmalonic acid was also obtained.

22. An attempted reaction of sodium caproate with n-amylsodium.

In the three experiments which follow, the sodium caproate was formed by adding 6.3 g. of n-caproic acid in 15 cc. of ligroin to the n-amylsodium which was prepared under slightly varying conditions.

In experiment 1, 33 g. (0.31 mole) of n-amyl chloride in 25 cc. of ligroin was added to 17.5 g. (0.76 g. atom) of sodium sand in 150 cc. of ligroin over a period of two hours after which the mixture was stirred for one-half hour at 28°. The n-caproic acid was added, and the mixture

was allowed to stir for an additional three minutes at the same temperature. Rapid carbonation was effected in the usual manner. The total yield of n-caproic acid was 9.8 g. The actual yield was 3.5 g. or 19.2%. The yields are based on a 40% production of n-amylsodium. No n-butylmalonic acid was found.

In experiment 2, the same quantities of materials were used with the n-amylsodium being stirred for one hour at 28° after the addition of the n-amyl chloride. The n-caproic acid was added over a period of fifteen minutes and stirring was continued at 28° for three hours. The mixture was carbonated rapidly and the total yield of n-caproic acid was 11.9 g. The actual yield was 5.6 g. or 31%. No n-butylmalonic acid was isolated.

In experiment 3, 50 g. (0.47 mole) of n-amyl chloride in 40 cc. of ligroin was added to 26.3 g. (1.1 g. atom) of sodium sand in 150 cc. of ligroin over a period of two hours and forty-five minutes and then allowed to stir for fifteen minutes. The n-caproic acid was added over a period of two minutes, the mixture stirred at room temperature for sixty-two hours and then carbonated rapidly. The mixture was worked up as in the previous sixty-two hour equilibrium experiment. The total yield of n-caproic acid was 11.9 g. or actually 5.6 g. (31%). No n-butylmalonic

acid could be found but 0.79 g. of the acid melting at 183-184° was isolated.

23. An attempt to metalate cyclohexane with phenylsodium.

Into the usual apparatus (200 cc.) was placed a mixture of 22.5 g. (0.2 mole) of chlorobenzene, 11.5 g. (0.5 g. atom) of sodium sand and 130 cc. of cyclohexane. The reaction did not start after four hours of stirring at room temperature and then heating was started. After three and one-half hours the color test was still negative but was very positive after two more hours. The mixture was stirred twenty-four hours longer and carbonated by pouring on crushed solid carbon dioxide. The yield of benzoic acid was 4.2 g. or 17.4%. Hexahydrobenzoic, phthalic and terephthalic acids were absent.

24. An attempt to prepare cyclohexylsodium.

To a mixture of 11.5 g. (0.5 g. atom) of sodium sand in 100 cc. of cyclohexane was added 23.7 g. (0.2 mole) of cyclohexyl chloride over a period of twenty minutes. The mixture turned black after six hours of stirring and color tests at regular intervals were all negative. The reaction was considered negative when no color test was obtained after three additional hours of stirring.

25. An attempt to metalate methylcyclohexane with phenyl-sodium.

A solution of 22.5 g. (0.2 mole) of chlorobenzene in 30 cc. of methylcyclohexane was added to 11.5 g. (0.5 g. atom) of sodium sand in 100 cc. of methylcyclohexane. The reaction started after three hours, as was indicated by a positive color test, and was allowed to stir for thirty hours at room temperature. The black suspension was heated at 135° for three and one-half hours, no color changes being observed. Subsequent to carbonation the reaction was worked up in the usual manner. The yield of benzoic acid was 12.9 g. (52.5%); 1.9 g. (12.3%) of biphenyl was isolated and 5.1 g. of chlorobenzene was recovered.

26. Preparation of 1-methylcyclohexene. 85

A mixture of 500 g. (4.4 moles) of 1-methylcyclohexanol and 20 cc. of concentrated sulfuric acid (sp. gr. 1.84) was placed in a one-liter flask equipped with a three-foot fractionating column. Distillation was continued by heating with a free flame until only a small residue remained and the temperature began to rise. The 1-methylcyclohexene comes over mostly at 95°. The water was separated from the distillate and the hydrocarbon layer was washed twice with five per cent sodium hydroxide, twice with cold water and then dried over calcium chloride. It was then distilled

85. Private communication with Mr. W. Hartman of the Eastman Kodak Co.

through a Glinzky column and 316 g. (75%) of 1-methylcyclohexene was collected between 108-110°. The product was dried over sodium prior to further use.

27. Preparation of 3-methylcyclohexene. 85

The exact quantities and procedure were used as in the preparation of 1-methylcyclohexene with the exception that 4-methylcyclohexanol was substituted for the 1-methylcyclohexanol. The crude product was distilled through a Glinzky column at 103-104° and 311 g. (74%) of the hydrocarbon was obtained which was also dried over sodium.

28. An attempt to metalate 1-methylcyclohexene and 3-methylcyclohexene with phenylsodium.

To 5.7 g. (0.25 g. atom) of sodium sand prepared directly in 96 g. (1 mole) of the hydrocarbon was added 11.2 g. (0.1 mole) of chlorobenzene. Eight minutes after the addition of the chlorobenzene, the shiny sodium sand began to take on a black coating and the temperature started to rise. The temperature was not allowed to exceed 35-40° for three hours, and then it began to fall. The color test was positive. The suspension was refluxed for two hours and then carbonated in the usual manner. Some of the sodium metal which had melted into lumps was removed and the reaction mixture cautiously hydrolyzed with water. After

obtaining the solid acid and performing an extensive fractional crystallization from hot water, only benzoic acid could be isolated. The yields of benzoic acid in the 1-methylcyclohexene and 3-methylcyclohexene runs were 7.1 g. (58%) and 7.3 g. (58%), respectively.

29. An attempt to metalate *n*-propylbenzene with phenylsodium.

The sodium sand was prepared directly in 70 cc. of *n*-propylbenzene and to this was added 11.2 g. (0.1 mole) of chlorobenzene. The temperature started to rise after two hours of stirring and was kept between 35-40° for three hours after which the temperature dropped to 28°. Stirring was continued for twelve hours and then the suspension was heated at 100° for one hour. The reaction was cooled and then carbonated by pouring on crushed solid carbon dioxide. The sodium metal was cautiously hydrolyzed with water and the mixture subjected to steam distillation. The alkaline residue was extracted twice with ether and then the dissolved ether expelled by warming. Upon acidification, a viscous, brown acidic oil separated which was extracted with chloroform. The extract was heated with Norite for eight hours, filtered, and the chloroform removed by distillation. The residual oil was dissolved in dilute sodium carbonate solution, which was extracted with ether, and then acidified. An oil again precipitated. The total weight of the oil,

having a strong phenylacetic odor, was 3.4 g. An attempt was made to convert the acid to the possible α -phenylbutyramide but the tar which was obtained could not be resolved into a definite compound.

30. Metalation of β -methylnaphthalene.

The phenylsodium was prepared from 5.7 g. (0.25 g. atom) of sodium sand and 11.2 g. (0.1 mole) of chlorobenzene in 100 cc. of benzene. To the phenylsodium was added 28.4 g. (0.2 mole) of β -methylnaphthalene. No reaction was evident after stirring at room temperature for one hour. The mixture was then refluxed for twenty-one hours, carbonated and worked up in the customary manner to yield 0.8 g. or 4.3% of β -naphthylacetic acid melting at 137-138°. ¹⁸

31. An attempt to metalate α -methylnaphthalene with phenylsodium.

Practical Eastman α -methylnaphthalene was purified by drying with calcium chloride, distilling at 235-236.5° and then distilling from over sodium metal at 240-241°. The boiling point given in the literature is 241-242°. Several attempts to metalate this material, under varying conditions, resulted in the isolation of benzoic acid and a dark brown tar which could not be purified.

32. Metalation of mesitylene with phenylsodium.

Into the usual apparatus was placed a mixture of 140 cc. of pure, dried mesitylene, 11.5 g. (0.5 g. atom) of sodium sand and 22.5 g. (0.2 mole) of chlorobenzene. The reaction started in fifteen minutes and the temperature was kept at 35-40° for three hours. A black suspension formed which was then refluxed for two hours and immediately on the start of heating a brown color began to appear. Carbonation was effected by pouring the mixture on crushed solid carbon dioxide and then worked up in the usual way. On acidification of the alkaline layer the acidic material separated in the form of an oil. This oil upon extraction and crystallization from about 800 cc. of water gave 3.3 g. (20%) of 3,5-dimethylphenylacetic acid which melted at 95-97°. The melting point was elevated to 99-100° after two additional crystallizations from water. Nine grams of tarry oil was also isolated but could not be resolved into a definite substance. ¹⁸

33. An attempt to metalate pseudocumene with phenylsodium.

The sodium sand was prepared from 5.7 g. (0.25 g. atom) of metal directly in 80 cc. of purified pseudocumene. To this was added 11.2 g. (0.1 mole) of chlorobenzene and stirring was continued for three and one-half hours before

the reaction started. The mixture was allowed to stir at 30° for fifteen hours and then heated for ten hours. The black suspension was cooled, carbonated and worked up in the usual manner. Filiform crystals separated on cooling the acidified solution and an oil also deposited. The crystals were dissolved by heating the solution and were separated from the oil by filtration. The oil was further extracted with hot water and the extracts deposited 1.4 g. of yellowish hexagonal crystals on cooling. An attempt to decolorize 0.7 g. of the crystalline material by boiling with Norite ended in a complete adsorption of the acid by the charcoal from which it could not be extracted. The recrystallized material melted at 158-159°. The neutral equivalent was 146, but as yet no compound has been found to correspond with this value.

34. An attempt to metalate t-butylbenzene with phenylsodium.

To a mixture of 60 cc. of t-butylbenzene and 2.9 g. (0.125 g. atom) of sodium sand was added 5.6 g. (0.05 mole) of chlorobenzene. The reaction started after eighteen hours of stirring at 32° and then heated at 155° for nineteen hours. There was only a slight color test at the end of this time. After carbonating and working up the reaction mixture in the usual manner, 0.2 g. of benzoic acid was obtained as the only acidic material. Two grams of

biiphenyl was obtained and the unreacted t-butylbenzene was recovered.

35. An attempt to metalate isopropylbenzene with phenyl-sodium.

The mixture of 11.5 g. (0.5 g. atom) of sodium sand, 22.5 g. (0.2 mole) of chlorobenzene and 125 cc. of iso-propylbenzene started to react after one and one-half hours of stirring. The temperature suddenly rose to 100° but was immediately brought down to 28° by a cooling bath and stirred at this temperature for twelve hours. The suspension was heated for four hours, then carbonated and worked up in the usual manner. On repeated fractional crystallizations no dimethylphenylacetic acid could be isolated from the 8.7 g. (11.2%) of impure benzoic acid which melted at 118-120°. The benzoic acid was checked by a mixed melting point with an authentic sample.

36. Thermal stability of phenylsodium.

Two parallel preparations of phenylsodium were made from 100 cc. of benzene, 2.5 g. (0.1 g. atom) of sodium slices and 5 g. (0.014 mole) of diphenylmercury. Each of the two runs was stirred at room temperature for four and one-half hours; then one of the preparations was stirred at reflux temperature and the other at room temperature for twenty-four hours. The reactions were carbonated by

pouring on an ether slush of crushed solid carbon dioxide. Each of the runs was worked up in the usual manner with the inclusion of the usual tests for phthalic and terephthalic acids but only benzoic acid could be found. The yield of benzoic acid from the heated mixture was 2.13 g. or 62% and 2.96 g. or 86% from the run at room temperature. ¹⁸

37. An attempt to metalate biphenyl with phenylsodium.

Phenylsodium was prepared in the usual manner from 5.7 g. (0.25 g. atom) of sodium sand, 11.2 g. (0.1 mole) of chlorobenzene in 100 cc. of dried benzene and allowed to stir overnight at room temperature. To the black suspension was added 18.5 g. (0.12 mole) of dried biphenyl. The mixture was refluxed for a period of ten hours and then cooled, carbonated and worked up in the usual manner. A dark oil separated on acidification which upon extraction with hot water yielded 6.3 g. (52%) of benzoic acid as the only acid.

38. An attempt to metalate bi-o-tolyl with n-butylsodium.

Into the usual apparatus (100 cc.) was placed a mixture of 20 cc. of ligroin, 7.3 g. (0.023 mole) of di-n-butylmercury and 3 g. (0.13 g. atom) of sodium slices. The reaction started immediately and became a very dark grey suspension which was allowed to stir for one hour.

To this was added 3 g. (0.165 mole) of bi-o-tolyl and allowed to stir at room temperature for twenty-four hours. After cooling, the mixture was carbonated by pouring on solid carbon dioxide. The only acidic material which was obtained smelled of n-valeric acid. The n-valeric acid was removed in a vacuum as indicated in Figure 1, and two flakes of an acidic compound, melting at 136-138°, were obtained. Also, 0.8 g. of acidic tar remained.

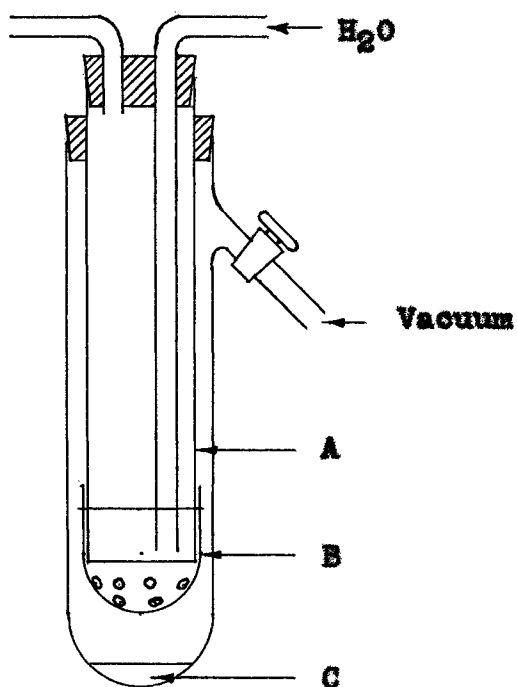


Figure 1

The apparatus indicated by Figure 1 was designed for the purpose of removing volatile aliphatic acids such as n-butyric and n-valeric from non-volatile acids. The principle involved is simply one of distillation in which the acids that condense on the "cold-finger," (A), are absorbed by the Soxhlet extraction cup, (B), instead of being allowed to drip back into the non-volatile acid at C. This separation was accomplished most successfully at a low pressure.

39. The reaction of phenylsodium with chlorobenzene.

The phenylsodium was prepared from 3 g. (0.13 g. atom) of sodium slices, 7.08 g. (0.02 mole) of diphenylmercury and 75 cc. of benzene in the usual manner. After amalgamating the residual sodium by the cautious addition of mercury, the phenylsodium suspension was decanted into a similar apparatus and 4.5 g. (0.04 mole) of chlorobenzene was added. The temperature immediately rose to 43° and started to drop after ten minutes. Color tests were made at regular intervals on the stirred mixture and after eight hours the test had become so faint that it was called negative. The mixture was hydrolyzed with water and the benzene layer yielded 1.9 g. or 61.7% of biphenyl; 0.4 g. of chlorobenzene was recovered and also 0.6 g. of tar which would not distil.

40. The reaction of p-tolylsodium with iodobenzene.

The usual apparatus (1000 cc.), with the addition of a dropping funnel, was used in this experiment. In the flask was placed 200 cc. of dried toluene, 23 g. (1.0 g. atom) of fine sodium sand and one-fifth of the 63.25 g. (0.5 mole) of p-chlorotoluene which was to be added during the course of the reaction. The temperature was kept between 35-40° by cooling with an ice-bath and when the temperature began to subside, due to completeness of reaction, 100 cc. more toluene was added. The rest of the halide was added over a period of one and one-half hours and then allowed to stir very vigorously for four more hours. At the end of this time 100 cc. of toluene was added to the pitch-black mixture followed by 105 g. (0.51 mole) of iodobenzene added over a period of forty-five minutes with the temperature being controlled between 30-40°. The stirring was continued for seventy-two hours, at the end of which only a slight color test was obtained. Carbonation was accomplished by pouring on solid carbon dioxide and the layers were then separated and worked up in the usual manner. The alkaline layer yielded 0.41 g. (0.6%) of p-toluic acid. The neutral layer was dried with calcium chloride and the toluene removed by fractionation through a twenty-inch Vigreux column. The remaining oil

was fractionally distilled in a vacuum and 27.5 g. of product boiling at 184-190°/76 mm. was obtained. There was practically no fore-run and 33 g. of tarry material remained in the Claisen flask. The 27.5 g. of oil was distilled at ordinary pressure and 14.5 g. (17.3%) of p-methylbiphenyl, boiling at 267-269°, was obtained.

41. The reaction of p-tolylsodium and bromobenzene.

The exact procedure as given above was followed in this experiment with the exception that 82 g. (0.52 mole) of bromobenzene was used in place of the iodobenzene. The color test was negative after forty-eight hours of stirring. The yield of p-methylbiphenyl was 10 g. or 12%.

42. Metalation of t-butylbenzene with n-butylsodium.

n-Butylsodium was prepared from 6.3 g. (0.02 mole) of di-n-butylmercury and 5.7 g. (0.25 mole) of sodium wire in 80 cc. of unsaturate-free ligroin. The mixture was stirred for four hours and then 4.02 g. (0.03 mole) of t-butylbenzene was added, allowed to stir at room temperature for twenty-eight hours, and then carbonated by pouring on solid carbon dioxide. The alkaline layer was acidified and placed on the hot-plate to evaporate slowly. By this process the n-valeric acid was removed and the remaining solid organic acid was separated from the inorganic salts by extraction

with ether. The ether was evaporated and the acid was crystallized three times from dilute ethyl alcohol; 0.81 g. (11.4%) of p-t-butylbenzoic acid, melting at 163-164° was obtained. A mixed melting point with p-t-butylbenzoic acid, obtained from the interconversion of p-bromo-t-butylbenzene, showed no depression.

Anal. Calcd. for $C_{11}H_{14}O_2$: neut. equiv., 178;

Found: neut. equiv., 175.

Another experiment upon the metalation of t-butylbenzene was performed with a few changes in conditions. Only 50 cc. of ligroin was used in this run and the time of stirring was increased to sixty-eight hours. No odor of n-valeric acid was perceptible from the acidified alkaline layer and it was extracted with ether, the extracts yielding 6.1 g. (86%) of acidic material. This acidic material was a mixture of isomeric t-butylbenzoic acids as the melting point was 90-140° and the found neutral equivalent was 176 as compared with the calculated value of 178. The acids could not be separated by fractional crystallization.

A three-gram sample of these mixed acids was oxidized by alkaline potassium permanganate. Upon resolving the acids, no benzoic acid could be isolated, indicating the absence of lateral metalation. No phthalic acid was obtained, but a mixture of high melting acids, terephthalic and most probably isoterephthalic acid, was obtained

indicating meta metalation in addition to para metalation.

43. Metalation of β -methylnaphthalene with n-butylsodium.

Into the usual apparatus (200 cc.) was placed a mixture of 50 cc. of ligroin, 6.3 g. (0.02 mole) of di-n-butylmercury and 5.7 g. (0.25 g. atom) of sodium wire. The reaction started immediately and was vigorously stirred for two hours. To this brown suspension was added 10 g. (0.07 mole) of β -methylnaphthalene. The suspension assumed an intense red color in a few minutes and gave a strong color test. The mixture was allowed to stir for twenty-six hours after which it was rapidly carbonated. After removing the suspension from the amalgam it was hydrolyzed and worked up in the usual manner. On acidification there was a faint odor of n-valeric acid which was removed from the solid acid by heating in the vacuum distillation apparatus described on page 94. After this treatment the acid was crystallized once from hot water and 2.3 g. or 31% of β -naphthylacetic acid, melting sharply at 140-141^o, was obtained.¹⁸

Anal. Calcd. for $C_{12}H_{10}O_2$: neut. equiv., 186;

Found: neut. equiv., 185, 186.

There is a little doubt about the purity of the di-n-butylmercury, and higher yields of the acid may be obtained if the mercurial is freshly distilled before use.

44. Metalation of α -methylnaphthalene with \bar{n} -butylsodium.

This experiment was performed in a manner identical to the one above. The same intense red color appeared when the α -methylnaphthalene was added as in the case of the β -methylnaphthalene but only a small amount, 0.9 g., of very impure acidic material was obtained. There was very little odor of \bar{n} -valeric acid and the mixture of acids could not be separated by any of the ordinary methods. It was decided that the mixture was most probably a result of nuclear as well as lateral metalation.

B. Potassium Compounds

1. A preparation of benzylpotassium from chlorobenzene, potassium and toluene.

Into the usual apparatus (500 cc.) was placed a mixture of 8.5 g. (0.22 g. atom) of potassium sand and 100 cc. of toluene to which a solution of 11.2 g. (0.1 mole) of chlorobenzene in 50 cc. of toluene was added very slowly, the temperature being kept between 30-35°. Since there was no induction period the temperature started rising with the addition of the first few drops of chlorobenzene. Occasional cooling with an ice-bath was necessary. The average time for the addition of the chlorobenzene was found to be one and one-half hours, and at the conclusion

of this preliminary operation the reaction mixture was refluxed for one hour, during which the color changed from a black to a brilliant brick-red. On completion of the refluxing, the mixture was cooled and poured jet-wise upon solid carbon dioxide. The yield of pure phenylacetic acid was 11.2 g. or 82%. No phenylmalonic acid could be isolated.

The above procedure was checked by Dr. O. Baine of Southwestern College with very close agreement in the yields. Using the same quantities of materials he was able to obtain 11.1 g. or 81.6% of phenylacetic acid.¹⁸

The above directions are the best of a series of runs all of which gave lower yields when conditions of temperature, time and quantity of solvent were varied.

2. Metalation of toluene with phenylpotassium.

Into the usual apparatus (200 cc.) was placed 5 g. (0.016 mole) of di-n-butylmercury and 3 g. (0.077 g. atom) of potassium in 50 cc. of sodium-dried benzene. The mixture was stirred for sixty-one hours at room temperature and then an aliquot was carbonated. This test portion gave only benzoic and no n-valeric acid, indicating that all the n-butylpotassium had been converted to phenylpotassium. To the dark suspension was added 50 cc. of dried toluene, refluxed for six hours and then carbonated by pouring on

solid carbon dioxide. The larger lumps of potassium amalgam were removed from the carbonation mixture by filtering through a coarse wire gauze. The reaction mixture was cautiously hydrolyzed in sequence by n-butyl alcohol, ethyl alcohol and water. The acidified layer yielded 1.9 g. or 44% of phenylacetic acid.¹⁸

3. Migration of potassium in p-tolylpotassium.

To a mixture of 7.7 g. (0.02 mole) of di-p-tolylmercury in 160 cc. of ligroin was added 7.8 g. (0.2 g. atom) of potassium metal. After refluxing for one and one-half hours the suspension started to take on a pink color and was stirred rapidly at this temperature for twelve hours. Subsequent to carbonation the reaction mixture was worked up in the usual manner. The yield of pure phenylacetic acid was 0.9 g. or 16.5%.¹⁸

4. Slow carbonation of benzylpotassium.

A 0.1 mole run of benzylpotassium was prepared in the usual manner. Gaseous carbon dioxide was passed over the stirred surface at such a rate that in fifteen minutes a negative color test was obtained. Stirring was continued for an additional hour and then the reaction was worked up in the usual manner. The yields of acids obtained were as follows: phenylacetic acid, 7.5 g. or 55%; phenylmalonic acid, 2.1 g. or 23%.¹⁸

5. An attempt to prepare phenylpotassium.

To a mixture of 7.4 g. (0.19 g. atom) of potassium sand in 100 cc. of toluene, cooled to 0°, was added 11.2 g. (0.1 mole) of chlorobenzene in 45 cc. of toluene at such a rate that the temperature at no time rose above 0°. The time required for the addition in this orienting experiment was four and one-half hours. Carbonation, at the end of this time, gave 7.3 g. or a 60% yield of phenylacetic acid. On concentration of the mother liquors from the crystallization of an aliquot of the total acidic material, no benzoic acid could be isolated.¹⁸

6. An attempt to trap phenylpotassium in cyclohexane.

To a mixture of 8.5 g. (0.22 g. atom) of potassium sand in 125 cc. of cyclohexane was cautiously added 11.2 g. (0.1 mole) of chlorobenzene. In one hour the temperature rose from 32° to 36° and after fifteen minutes more it again dropped back to 32°. No color test could be obtained after four more hours of stirring. The reaction was considered negative after heating at 85° for one and one-half hours produced a dark coloration on the potassium metal, but did not give a color test.

7. Preparation of diphenylbenzylcarbinol.

To benzylpotassium prepared in the usual manner from potassium, 0.1 mole of chlorobenzene and toluene, was added 18.2 g. (0.1 mole) of benzophenone, in 50 cc. of toluene, over a one and one-half hour period. The brick-red color slowly disappeared and the solution assumed a deep emerald-green color, possibly due, in part, to the formation of the potassium ketyl of benzophenone. The temperature was not allowed to exceed 40°, and the mixture was allowed to stir for one hour after the temperature ceased rising. The neutral layer was prepared in the usual manner and then the toluene removed by distilling through a fractionating column. The residue solidified on cooling and was crystallized from ligroin yielding 22 g. or 59% of diphenylbenzylcarbinol melting at 87-88°. ¹⁸

8. Preparation of 3,5-dimethylbenzylpotassium.

To a mixture of 8.5 g. (0.22 g. atom) of potassium sand and 100 cc. of dry mesitylene was slowly added a solution of 11.2 g. (0.1 mole) of chlorobenzene in 39 cc. of mesitylene. The time of addition was one and one-half hours, and the temperature was kept between 30-35°. The black suspension changed slowly to the characteristic brick-red color upon refluxing for one hour. After

carbonation with solid carbon dioxide and hydrolysis, there was isolated 13 g. or a 79% yield of 3,5-dimethylphenylacetic acid which melted at 99.5-101°. ¹⁸

9. Slow carbonation of 3,5-dimethylbenzylpotassium.

A run of 3,5-dimethylbenzylpotassium was prepared as above and then carbonated by slowly passing gaseous carbon dioxide over the surface of the stirred suspension. The yield of 3,5-dimethylphenylacetic acid was 30%. In addition, there was obtained a 15% yield of 3,5-dimethylphenylmalonic acid which softened at 149-150° and melted with decomposition at 154-155°. ¹⁸

Anal. Calcd. for $C_{11}H_{12}O_4$: neut. equiv., 104; C, 63.46; H, 5.77. Found: neut. equiv., 106, 107; C, 63.55, 63.57; H, 5.85, 5.81.

10. An attempt to metalate pseudocumene with the potassium-chlorobenzene system.

To 8.5 g. (0.22 g. atom) of potassium sand in 100 cc. of pseudocumene was added a solution of 11.2 g. (0.1 mole) of chlorobenzene in 40 cc. of pseudocumene over a period of two hours, the temperature being kept between 35-40°. The reaction was allowed to stir for an additional fifteen minutes and then refluxed for ten minutes. The suspension gave a slight color test, was carbonated and worked up in the usual manner. No acids could be isolated.

11. An attempt to prepare phenylisopropylpotassium.

The experiment was performed in a manner directly analogous to the preceding one with the exception that 160 cc. of isopropylbenzene (cumene) was used. The same negative results were also obtained.

C. Lithium Compounds

1. An attempted reaction of bromobenzene with lithium in toluene.

No test for an organometallic compound could be obtained after stirring a mixture of 31.4 g. (0.2 mole) of bromobenzene, 3 g. (0.43 g. atom) of lithium and 100 cc. of toluene for several hours.

2. An attempted reaction of iodobenzene with lithium in toluene.

The same negative results were obtained in this run when 40.8 g. (0.2 mole) of iodobenzene was substituted for the bromobenzene as in the preceding experiment.

3. An attempt to metalate toluene with phenyllithium.

A solution of phenyllithium was prepared from 31.4 g. (0.2 mole) of bromobenzene and 3 g. (0.43 g. atom) of lithium in 100 cc. of diethyl ether. After filtering, the ether was carefully evaporated, 175 cc. of toluene added

and then the mixture was refluxed for three hours. The suspension, which took on a slightly reddish color, was cooled, carbonated and worked up in the usual manner. Only benzoic acid was isolated.

4. An attempt to prepare benzyl lithium from benzyl chloride and lithium.

Into the usual apparatus (200 cc.) was placed 3 g. (0.43 g. atom) of lithium sand (prepared in dried mineral oil) and 100 cc. of dried toluene. To this was slowly added 25.4 g. (0.2 mole) of purified benzyl chloride. There was no temperature rise and the lithium sand took on a purplish color. Since the reaction mixture gave no color test after stirring for thirty-six hours, it was not carbonated.

5. The reaction of n-butyl bromide with lithium in toluene.

To a mixture of 3 g. (0.43 g. atom) of lithium sand in 110 cc. of toluene was added a solution of 27.4 g. (0.2 mole) of n-butyl bromide in 40 cc. of toluene. The reaction started after three and one-half hours of stirring. The suspension, which took on a cloudy appearance, was kept at 35-40° for one hour and then gently refluxed for fifteen hours. One and one-half hours after heating was started, the suspension changed to a definite orange color. Carbonation and preparation of the alkaline layer were

accomplished in the usual manner. On acidification a small amount of tarry oil separated, which had a slight odor of phenylacetic acid, and was extracted with hot water. A small amount, 0.02 g., of impure phenylacetic acid having a melting point of 65-72° was isolated.

6. The reaction of *n*-butyl chloride with lithium in toluene.

To 4.2 g. (0.6 g. atom) of lithium in 80 cc. of toluene was added 13.9 g. (0.15 mole) of *n*-butyl chloride in 20 cc. of toluene. The reaction started in fifteen minutes and the tendency for the temperature to rise was over in one and one-half hours. The suspension became reddish in color, was carbonated and worked up in the usual manner. No phenylacetic acid could be isolated from the 3.2 g. (24%) of *n*-valeric acid which was obtained.

7. The reaction of *n*-butyllithium with toluene.

n-Butyllithium was prepared from 3 g. (0.45 g. atom) of lithium, 27.4 g. (0.2 mole) of *n*-butyl bromide and 150 cc. of ether in the customary manner. The suspension was filtered, most of the ether removed by distillation and the last traces expelled by adding 50 cc. of toluene and again distilling at a higher temperature. To the cloudy suspension was added 50 cc. more toluene and then it was refluxed gently for five hours. After this time

the color had turned to a brilliant orange, however, after carbonating and working up the mixture in the usual manner, only a small amount of n-valeric acid and no phenylacetic acid could be isolated.

8. The reaction of n-butyllithium with toluene in ether.

To a filtered ether solution of n-butyllithium, prepared from 27.4 g. (0.2 mole) of n-butyl bromide, was added 180 cc. of toluene. Within five minutes after application of heat, a heavy white precipitate (probably lithium bromide) formed. After refluxing for nineteen hours, carbonation was effected by solid carbon dioxide, and the yield of phenylacetic acid was 0.06 g. or 0.22%.¹⁸

9. The reaction of ethyl chloride with lithium in toluene.

To 3 g. (0.43 g. atom) of lithium in 150 cc. of toluene was added 12.9 g. (0.2 mole) of ethyl chloride. The suspension was stirred for nine hours and then refluxed for two hours. After the first two hours as well as at the end of the reflux period, tests for an organometallic compound were positive. The mixture was carbonated and worked up in the usual manner. No phenylacetic acid could be isolated from the tarry oil which yielded 2.1 g. (15%) of propionic acid.

10. An attempt to prepare p-tolylithium.

Into the usual apparatus (200 cc.) was placed 1.4 g. (0.21 g. atom) of lithium metal in 40 cc. of ligroin. To this was added, in a dropwise manner, a solution of 17.1 g. (0.1 mole) of p-bromotoluene in 30 cc. of ligroin. The reaction was considered negative when no color test could be obtained after twenty-four hours of heating and stirring.

11. p-Tolylithium heated in mineral oil.

Into the usual apparatus (200 cc.) was placed a mixture of 1.4 g. (0.21 g. atom) of lithium metal and 40 cc. of diethyl ether to which was then added 40 drops of p-tolyl bromide. The remainder of the total of 17.1 g. (0.1 mole) of halide was dissolved in 40 cc. of diethyl ether and added fairly rapidly, allowed to stir at room temperature for one hour, and then filtered through glass wool. The ether was distilled and 80 cc. of potassium-dried mineral oil, boiling point 390-400°, was added. After heating at 200-220° for nineteen hours, the color test was still very positive and the suspension was cooled and carbonated. After hydrolysis the two layers formed an emulsion which could be broken only by allowing it to stand for a long period of time. The alkaline layer yielded 7.2 g. (53%) of p-toluic acid. There was isolated from the oily layer, by careful fractionation, 3.8 g. (41%) of toluene. No

phenylacetic acid could be found.

12. An attempt to prepare and then rearrange p-tollyllithium from the mercurial.

A mixture of 3.8 g. (0.01 mole) of di-p-tolylmercury, 80 cc. of dried ligroin and 1.4 g. (0.21 g. atom) of lithium metal was allowed to reflux for forty-eight hours. At the end of this time there was no perceptible reaction and the color test was negative.

13. An attempt to metalate toluene with n-butyllithium prepared from the mercurial.

Into the usual apparatus (200 cc.) was placed a mixture of 6.3 g. (0.02 mole) of di-n-butylmercury, 1 g. (0.145 g. atom) of lithium and 25 cc. of toluene. There was no change or color test after fifteen minutes of stirring at room temperature. Refluxing was started and in five minutes the color test was positive; after two hours of stirring the mixture changed from colorless to a deep reddish orange and was allowed to stir for an additional ten hours at a mild reflux. Carbonation was effected by pouring on crushed solid carbon dioxide and then worked up in the usual manner. A small amount of n-valeric acid, but no phenylacetic acid, was isolated.

For other attempted methods of preparing benzylolithium see the section entitled "Interconversions".

D. Calcium Compounds

1. An attempt to prepare benzylcalcium chloride.

To a mixture of 24 g. (0.6 g. atom) of calcium metal in 100 cc. of toluene was added 33.8 g. (0.3 mole) of chlorobenzene. When a negative color test was obtained at the end of fourteen hours of stirring at room temperature, the mixture was refluxed for sixty hours. No color test could be obtained at the end of this time and the reaction was considered negative.

2. An attempt to prepare p-tolylcalcium chloride.

To a mixture of 24 g. (0.6 g. atom) of calcium metal in 50 cc. of toluene was added 38 g. (0.3 mole) of p-chlorotoluene. Stirring and refluxing was carried on for seventy-two hours with no evidence of a reaction.

3. An attempt to prepare p-tolylcalcium bromide.

No reaction was perceptible after stirring a mixture of 24 g. (0.6 g. atom) of calcium metal, 50 cc. of toluene and 51.3 g. (0.3 mole) of p-bromotoluene for seventy-two hours.

E. Interconversions

1. The preparation of 2-bromodibenzothiophene.⁸⁶

To a solution of 55.2 g. (0.3 mole) of dibenzothiophene in 225 cc. of carbon tetrachloride was added one gram of iron filings. While the mixture was being stirred and gently heated, 48 g. (0.3 mole) of bromine was added over a two-hour period. Heating and stirring were continued for twenty-four hours and then the reaction mixture was cooled, washed free of excess bromine with sodium bisulfite solution and the layers separated. The carbon tetrachloride layer was washed carefully with sodium carbonate, water, and then dried over sodium sulfate. The solvent was removed by distillation and the residue twice distilled in a vacuum, boiling at 188°/ 3 mm. The distillate was crystallized three times from ethyl alcohol and finally subjected to mild vacuum sublimation in order to remove the last traces of dibenzothiophene. The yield was 27.6 g. or 35% of 2-bromodibenzothiophene melting at 124-125°.

2. Interconversion of 2-bromodibenzothiophene with n-butyl lithium.

Into the usual apparatus (200 cc.) was placed 100 cc. of dried ether, 3 g. (0.43 g. atom) of lithium chips and

86. Courtot, Nicolas and Liang, Compt. rend., 186, 1624 (1928).

to this was slowly added 27.4 g. (0.2 mole) of *n*-butyl bromide. The mixture was allowed to stir at room temperature for two and one-half hours. While the *n*-butyllithium was being prepared, another similar apparatus (500 cc.) was set up, and into it was placed 26.2 g. (0.2^{0.1} mole) of 2-bromodibenzothiophene in 125 cc. of dried benzene and 25 cc. of ether. The mixture was heated to 40° to effect solution, then cooled to room temperature and the filtered *n*-butyllithium was added. The reaction mixture immediately became an amber color and was refluxed very gently for six hours after which the color test was still positive. This was cooled, carbonated and hydrolyzed. The ether-benzene layer was distilled and the pasty residue was extracted with thirty per cent potassium hydroxide. After acidification and drying, 3.8 g. (17%) of acidic material was obtained having a melting point of 256-257°, that corresponded very well with 2-carboxydibenzothiophene which melts at 255-256°.

In order to eliminate the possibility of the compound being the 4-acid, the carbomethoxy compound was prepared by treating a small amount of the acid with diazomethane in ether solution. The resulting ester melted at 72° and a mixed melting point with an authentic sample⁸⁷ of 2-carbomethoxydibenzothiophene failed to show any depression.

⁸⁷. A sample of this ester was kindly provided by Dr. A. L. Jacoby.

3. The reaction of benzyl chloride with n-butyllithium.

n-Butyllithium was prepared in the usual manner from 13.7 g. (0.2 mole) of n-butyl bromide, 1.5 g. (0.22 g. atom) of lithium metal and 175 cc. of ether. The mixture was filtered and 8.23 g. (0.065 mole) of freshly distilled benzyl chloride in 35 cc. of ether was added through a dropping funnel at such a rate that very vigorous refluxing took place. After addition of all the chloride in three minutes, there remained a white precipitate. It should be mentioned that the color of the solvent changed from colorless to an amber-yellow and back again to colorless during the addition of the halide. The reaction mixture gave a very weak color test and was immediately carbonated. On separating and working up the alkaline layer, only a few drops of n-valeric acid were obtained. The ether layer was dried over calcium chloride and then distilled. The residual oil was fractionally distilled, 1.8 g. (31%) of bibenzyl (mixed melting point), 2.3 g. (24%) of n-amylbenzene, and 1.5 g. (26%) of n-octane as well as a tarry oil were obtained. The slightly impure n-amylbenzene was identified by a found refractive index of 1.493 as compared with the 1.491 value given in the literature. The n-octane was too impure to give a good refractive index measurement.

4. An attempted reaction of benzylnaodium with lithium bromide.

Benzylnaodium was prepared in the usual manner from 22.5 g. (0.2 mole) of chlorobenzene, 11.5 g. (0.5 g. atom) of sodium sand and 150 cc. of toluene. After the reaction was completed, the suspended material was allowed to settle and 115 cc. of the solvent was siphoned off. The removed solvent gave no color test. The benzylnaodium mixture was cooled to -10° and then 135 cc. of diethyl ether, which had also been cooled to -10° , was added. Immediately 20 g. (0.23 mole) of anhydrous lithium bromide was added and the mixture was allowed to stir very rapidly for one hour at -10° . The reddish-orange ether solution did not change in color. To check the absence of benzyl lithium, 18 g. (0.2 mole) of paraformaldehyde was added and the mixture allowed to stir for ten hours. (Benzyl lithium but not benzylnaodium undergoes an allylic rearrangement to form α -tolylcarbinol.) At the end of this time the mixture was hydrolyzed, low-boiling petroleum ether added and the layers separated. The residue obtained after removing the petroleum ether was distilled and 4.7 g. of a clear yellow oil, remindful of the essence of roses, was obtained at $88-93^{\circ}/5$ mm. Both α -tolylcarbinol and β -phenylethyl alcohol distil at this temperature so that it was necessary to prepare the α -naphthyl urethane.

The urethane obtained was that of β -phenylethyl alcohol and its purity, after one crystallization from carbon tetrachloride, indicated the absence of all but very small quantities of benzyl lithium.

In another run an attempt was made to filter the ether solution of benzyl sodium but since it was not conveniently possible to run the filtration at -10° , the benzyl sodium reacted with the ether and was destroyed.

5. An attempted interconversion of chlorobenzene with \bar{n} -butyl sodium.

A mixture of 12.6 g. (0.04 mole) of di- \bar{n} -butylmercury, 10 g. (0.43 g. atom) of sodium wire and 150 cc. of ligroin was stirred for twenty-nine hours at room temperature. The suspension of \bar{n} -butyl sodium was decanted from the excess sodium metal which had amalgamated into a large globule. On the addition of 4.5 g. (0.04 mole) of chlorobenzene in 10 cc. of ligroin, over a period of ten minutes, there was only a two degree rise in temperature and the color of the suspension changed from light brown to purple. Stirring was allowed to continue for thirty-five minutes and then carbonation was accomplished in the usual manner. Acidification and extraction of the alkaline layer yielded \bar{n} -valeric acid and a small amount of tar from which was sublimed .002 g. of acid melting at $119-120^{\circ}$. This was

most probably benzole acid, undoubtedly resulting from a reaction other than interconversion.

6. An attempted interconversion of d-chloronaphthalene with n-butylnsodium.

n-Butylnsodium was prepared from 6.28 g. (0.02 mole) of di-n-butymercury, 4 g. (0.174 g. atom) of sodium slices and 75 cc. of low-boiling petroleum ether. The suspension was transferred, under a liberal flow of nitrogen, to another 200 cc. three-necked flask on which had been etched a 100 cc. calibration mark. To this decanted suspension was quickly added 6.5 g. (0.04 mole) of d-chloronaphthalene and enough petroleum ether to bring the volume to 100 cc. Aliquots, having a volume of 25 cc., were removed and carbonated at intervals of 6, 12, 18 and 24 minutes. No d-naphthole acid was obtained and 4.7 g. (72%) of the d-chloronaphthalene was recovered.

7. An attempted interconversion of p-chlorotoluene with n-butylnsodium.

Into a 200 cc., three-necked flask was placed 5 g. (0.13 g. atom) of sodium slices. The flask was filled with nitrogen and then heated to a temperature just above the melting point of the sodium. A swirling motion was imparted to the flask as it cooled and the sodium was distributed evenly, in the form of a mirror, on the sides of

the flask. When the flask had cooled sufficiently, 75 cc. of ligroin and 6.28 g. (0.02 mole) of di-n-butylmercury were added and allowed to stir for seven hours. The n-butylsodium was transferred to a flask calibrated to a 100 cc. volume and 5.06 g. (0.04 mole) of p-chlorotoluene was added. Enough ligroin was added to bring the volume to 100 cc. and then 25 cc. aliquots were removed and carbonated at 2, 5, 10 and 15 minute intervals after the addition of the halide. No p-toluic acid was found on acidification of the alkaline layers.

8. Bromination of t-butylbenzene.⁸⁸

Into a 100 cc. bromination flask was placed a mixture of 30 g. of bromine and 0.5 g. of iodine. The mixture was refluxed for two minutes and then 25 g. (0.187 mole) of t-butylbenzene was added over a period of five hours while the flask was immersed in an ice-bath. A large volume of hydrogen bromide was evolved and the reaction mixture was allowed to stand for ten hours. Excess bromine and hydrogen bromide were removed by pouring the reaction mixture into sodium bisulfite solution. After washing with sodium hydroxide and water, the halogenated layer was dried with calcium chloride and then distilled. Only 2.5 g. (6.3%) of material was obtained which had the boiling point range, given in the literature, for p-bromo-t-butylbenzene.

88. Schramm, Monatsh., 9, 617 (1888).

9. The interconversion of p-bromo-t-butylbenzene with n-butyllithium.

Into the usual apparatus (200 cc.) was placed 25 cc. of filtered n-butyllithium solution containing approximately one gram of the organometallic and to it was added 2.5 g. (0.0117 mole) of pure p-bromo-t-butylbenzene. A yellow color appeared immediately. The solution was allowed to stir for thirty minutes after which it was carbonated and then worked up in the usual manner. The 1.8 g. (86%) of solid acidic material had a slight odor of n-valeric acid which disappeared after one crystallization from dilute ethyl alcohol. The p-t-butylbenzoic acid melted at 158-160° and a mixed melting point with the acid obtained from the metalation of t-butylbenzene with n-butylna was 159-161°.

10. The interconversion of bromomesitylene with n-butyllithium.

n-Butyllithium was prepared from 3 g. (0.43 g. atom) of lithium, 27.4 g. (0.2 mole) of n-butyl bromide and 250 cc. of ether. The suspension was filtered⁸⁹ through a sintered glass crucible and then diluted to 260 cc. By withdrawing a 10 cc. aliquot and titrating with standard acid, it was found that the 250 cc. of solution contained 0.111 mole or 7.1 g. of n-butyllithium. To the filtered, refluxing

89. Gilman, Langham and Moore, J. Am. Chem. Soc., 62, 2334 (1940).

solution was rapidly added 19.9 g. (0.1 mole) of mesityl bromide. Aliquots of 50 cc. volume were withdrawn, at the indicated periods of time, and carbonated with the following results:

TABLE XIX

The Interconversion of Bromomesitylene with n-Butyllithium

<u>Time</u> (Minutes)	<u>2,4,6-Trimethylbenzoic Acid</u>	
	<u>G.</u>	<u>%</u>
.5	.15	4.6
2.0	.32	9.7
5.0	.69	21.0
15.0	1.23	37.3
60.0	1.33	40.0

(Since apparently no maximum had been reached, the reaction was repeated and aliquots were again removed and carbonated.)

<u>Time</u> (Hours)	<u>2,4,6-Trimethylbenzoic Acid</u>	
	<u>G.</u>	<u>%</u>
1.0	1.28	39
1.25	1.09	33
1.50	.93	28
1.75	.91	27.5
2.00	.74	22

The maximum interconversion was obtained, and checked, at the end of one hour. The crude 2,4,6-trimethylbenzoic acid melted at 140-149° and after one crystallization from low-boiling petroleum ether it melted at 151°.

11. The interconversion of pseudocumyl bromide with n-butyllithium.

A solution of n-butyllithium was prepared from 45.7 g. (0.333 mole) of n-butyl bromide, 5 g. (0.725 g. atom) of lithium and 250 cc. of ether. After titration, and dilution of the filtered solution to 400 cc. it was found that 0.18 mole of n-butyllithium was present. To the clear solution was added 25 g. (0.125 mole) of pseudocumyl bromide, 50 cc. aliquots withdrawn and carbonated at the indicated periods of time with the following results:

TABLE XX

The Interconversion of Pseudocumyl Bromide with n-Butyllithium

<u>Time</u> <u>(Minutes)</u>	<u>2,4,5-Trimethylbenzoic Acid</u>	
	<u>G.</u>	<u>%</u>
3	.96	37.2
5	1.39	54.0
15	1.63	63.3
30	1.47	57.0
45	1.48	57.4
60	1.46	56.6

Continued on following page.

TABLE XX (Concluded)

<u>Time</u> <u>(Minutes)</u>	<u>2,4,5-Trimethylbenzoic Acid</u>	
	<u>G.</u>	<u>%</u>
75	1.39	54.0
90	1.34	52.0

The melting point of the acid as given in the literature should be 152°. The crude acid isolated, melted at 149-150° and at 151° after one crystallization. 2,4,6-Trimethylbenzoic acid also melts at 152° but a mixed melting point with 2,4,5-trimethylbenzoic acid was 110-118°.

12. The interconversion of d-bromonaphthalene with n-butylsodium.

A suspension of n-butylsodium was prepared from 6.3 g. (0.02 mole) of di-n-butylmercury, 3 g. (0.13 g. atom) of sodium metal and 100 cc. of ligroin. The n-butylsodium was removed from the amalgam by decantation into a similar nitrogen-filled flask and then 8.28 g. (0.04 mole) of d-bromonaphthalene was added in one portion. The temperature rose from 31° to 55° in three minutes. After cooling, 25 cc. aliquots were removed and carbonated at the following periods of time with the indicated results:

TABLE XXI

The Interconversion of α -Bromonaphthalene with n-Butylsodium

<u>Time</u> <u>(Minutes)</u>	<u>α-Naphthoic Acid</u>	
	<u>G.</u>	<u>%</u>
5	.45	26.2
10	.35	20.4
15	.13	7.6
20	.83	48.2

There is little uniformity in the values because it was difficult to pipette the coarse suspension of the organometallic mixture. The representative value should be the average of the four results, namely, 25.6%.

13. An attempted interconversion of benzyl chloride with phenylethynyllithium.

Phenyllithium was prepared from 0.6 g. (0.087 g. atom) of lithium, 6.28 g. (0.04 mole) of bromobenzene and 65 cc. of ether. To this solution was added 5.10 g. (0.05 mole) of phenylacetylene and stirring was allowed to continue for ten hours. The yield of phenylethynyllithium thus obtained was considered to be 68%.² The solution was filtered and 4.3 g. (0.034 mole) of benzyl chloride in 5 cc. of ether was added. There was no temperature rise. Stirring was continued at room temperature for three hours and at reflux temperature for one hour, then cooled,

carbonated and worked up in the usual manner. The total weight of phenylpropionic acid melting at 135-136° was 4.6 g. or 79% of the theoretical. Not even an odor of phenylacetic acid was obtained.

F. Allylic Rearrangements

1. The reaction of benzylnaodium with paraformaldehyde.

Benzylnaodium was prepared in the usual manner from 11.5 g. (0.5 g. atom) of sodium metal, 22.5 g. (0.2 mole) chlorobenzene and 150 cc. of toluene. To the prepared benzylnaodium mixture, 10 g. of paraformaldehyde was added in small portions. There was a definite temperature rise and the reaction was kept at room temperature with the aid of a water-bath. The color test was negative at the end of one hour and forty-five minutes. The mixture was allowed to stir for ten hours and then the toluene was distilled off as completely as possible, in a stream of nitrogen, the recovery being 140 cc. The excess sodium was destroyed by the cautious addition of 125 cc. of alcohol and then most of the alcohol was removed through a fractionating column. Dilute hydrochloric acid was added to the residue and the liberated oil extracted with ether. After drying the extracts with sodium sulfate the ether was removed and the residual oil was subjected to fractional

distillation. A total of 4.3 g. of clear yellow oil, boiling at 207-213^o, and having a very fragrant odor, was obtained. The oil could not be induced to form α -naphthyl urethane or phenyl urethane derivatives but on oxidation a small amount of benzoic acid, and no phthalic acid, was obtained. If the oil was β -phenylethyl alcohol, the yield was 17.7%.

This experiment was repeated using the method of Morton⁹⁰ with the result that only a 2% yield of oil, boiling 10^o below the boiling point of β -phenylethyl alcohol, was obtained.

2. The reaction of benzylsodium with acetic anhydride.

Benzylsodium was prepared as above and then the reaction mixture was slowly added to 48 cc. of acetic anhydride in 100 cc. of toluene. On working up the mixture in the usual manner and oxidizing the residual oil with alkaline potassium permanganate, only benzoic acid could be found.

3. Preparation of dibenzylmercury.⁹¹

Benzylmagnesium chloride was prepared by slowly adding 80 g. (0.63 mole) of benzyl chloride in 180 cc. of ether to a mixture of 15.3 g. (0.63 g. atom) of magnesium

90. Morton and Falwell, J. Am. Chem. Soc., 60, 1430 (1938).

91. Wolff, Ber., 46, 64 (1913).

turnings in 560 cc. of ether. At the end of three hours of stirring, 85.6 g. (0.32 mole) of dried mercuric chloride was added in small portions. After one hour of stirring the reaction mixture began to assume a white, viscous state and 150 cc. more ether was added and stirring continued for eight hours. The white mass was poured into dilute hydrochloric acid with the formation of a grey sludge. The sludge was extracted with two liters of ether and then all the ether layers were combined, dried over calcium chloride and filtered. The mixture of dibenzylmercury and benzylmercuric chloride remained as a crystalline residue on evaporation of the ether. This residue melted at 90-105°.

A solution of sodium stannite⁸³ was prepared by adding a solution of 25 g. of sodium hydroxide in 125 cc. of water to 12 g. of hydrated stannous chloride in 125 cc. of water and then filtering. To the filtered solution was added the crude mixture of mercurials and the suspension turned a very dark grey. The reaction mixture was allowed to stir for three hours, filtered, and the residue dried after washing with water. The dibenzylmercury was extracted with 1500 cc. of acetone and then the solvent was distilled until only 150 cc. remained. On cooling to -12°, 34 g. (28%) of dibenzylmercury, melting at 110-110.5° (Lit. 111°), was obtained.

4. The reaction of authentic benzylsodium³⁹ and formaldehyde.

Into a 250 cc. Schlenk tube was placed a mixture of 7.7 g. (0.02 mole) of dibenzylmercury, 150 cc. of dried benzene and 11.5 g. (0.5 g. atom) of sodium wire. The tube was sealed and placed on the shaking machine where it remained for five days during which a brick-red suspension of benzylsodium formed. Part of the benzene was decanted and then all but 10 cc. distilled off in a stream of nitrogen. Two hundred cubic centimeters of dried ether, cooled to -12° , was used to take up the benzylsodium. The deep-red suspension was decanted into the usual type of apparatus (500 cc.) which was kept in a freezing bath. Formaldehyde was immediately passed over the stirred surface, the red color disappeared in five minutes but it was nine hours before a definitely negative color test could be obtained. The ether layer was worked up in the usual manner and one and one-half grams of somewhat fragrant oil remained. On oxidation only benzoic acid and no phthalic acid could be found. A mixed melting point with authentic benzoic acid gave no depression.

5. Carbonation of authentic benzylsodium.

Instead of using the recommended Schlenk tube the usual apparatus was used in which to prepare benzylsodium

from 7.7 g. (0.02 mole) of dibenzylmercury, 150 cc. of benzene and 11.5 g. (0.5 g. atom) of sodium sand. The mixture was stirred for thirty-six hours and then poured on crushed solid carbon dioxide. The yield of phenylacetic acid (mixed melting point) was 4.6 g. or 84% of the theoretical.

6. Effect of temperature on the allylic rearrangement of benzylmagnesium chloride.

A solution of 38.1 g. (0.3 mole) of benzyl chloride in 50 cc. of di-n-butyl ether was prepared and then added as indicated to the magnesium metal.

To a mixture of 7.5 g. (0.3 g. atom) of magnesium turnings and 50 cc. of di-n-butyl ether was added 20 cc. of the diluted halide. The reaction mixture was allowed to stir for five hours during which it failed to start, even when a few iodine crystals were added. However, when 50 cc. of diethyl ether was added the reaction became very vigorous and had to be cooled with an ice-bath. The remaining halide was diluted with 50 cc. more of di-n-butyl ether and then added slowly to the reaction mixture. A possible complex-formation between the diethyl ether and Grignard reagent was evidenced by the fact that less and less refluxing occurred as the reaction proceeded, even as the temperature rose. The reaction was stirred for one hour after addition of the halide and then allowed to

settle overnight. The supernatant solution of the Grignard reagent was filtered through a sintered glass crucible and then diluted to 410 cc. with di-n-butyl ether. The filtered solution contained 0.43 mole of Grignard and was then divided into two 200 cc. portions.

Formaldehyde gas, generated from 10 g. of paraformaldehyde, was admitted to the stirred surface of one of the Grignard portions at 15-20°. This reaction will be designated as A. To the other portion, B, the same quantity of formaldehyde gas was admitted at 90°, the reflux temperature of the mixture.

Runs A and B were treated identically in the following manner. After pouring the reaction mixtures on cold dilute sulfuric acid, the layers were separated and the ether layer washed twice with water. The aqueous layer and water extracts were combined and then extracted with ether which was added to the original ether layer. The solvent was removed and the residue vacuum distilled.

7. Results of run A.

At 110-112°/12 mm., 0.8 g. of clear oil came over which would not form an α -naphthyl urethane derivative. At 115-130°/6 mm., 2.8 g. (10.5% based on the titration) of o-tolylcarbinol, melting at 50-51°, was obtained. A mixed melting point with the o-tolylcarbinol of Dr. J. E. Kirby gave no depression.

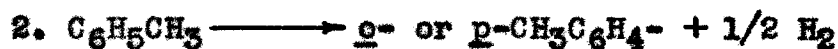
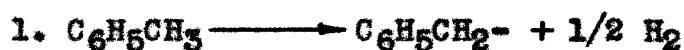
8. Results of run B.

At 110-114^o/12 mm., 4.6 g. of clear oil was obtained which could not be fractionated and which could not be induced to crystallize. Its content of o-tolylcarbinol was obtained by converting it to the α -naphthyl urethane. A weight of 3.6 g. of derivative, equivalent to 1.5 g. of o-tolylcarbinol was obtained. At 115-130^o/6 mm., 3.4 g. of crystalline o-tolylcarbinol (mixed melting point) was obtained. The total yield of rearrangement product was therefore 4.9 g. or 18%.

In runs A and B there remained after vacuum distillation a large quantity of black oil which was thought to be a "formal" of some of the alcohols which were produced. However, after many hours of refluxing in an attempt to hydrolyze the substance, no alcohols could be found. An oil distilled at 150 to 210^o, but did not form phenyl- or α -naphthyl urethanes.

IV. DISCUSSION

The fundamental and enlightening work of Hein⁹² on the exclusive formation of free benzyl radicals when toluene is thermally decomposed provides the basis for a hypothesis concerning the formation of lateral organoalkali compounds at elevated temperatures. According to the research work just mentioned, there exist three different free radical possibilities when toluene is "split" at a high temperature and low pressure, (900-1100° and 0.1-0.5 mm.).

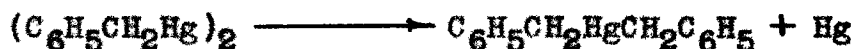


Using the apparatus of Rice,⁹³ the free radicals which resulted from the thermolysis were captured in mercury vapor and it is possible that the reactions which took place occurred as follows:



The substance $(\text{C}_6\text{H}_5\text{CH}_2\text{Hg})_2$ is stable at the temperature of liquid air and decomposes to dibenzylmercury on warming to room temperature:

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92. Hein and Mesé, Naturwissenschaften, 26, 710 (1938).
93. Rice, F. O., "The Aliphatic Free Radicals", Johns Hopkins Press (1935).



Identification of the compound formed was carried out by reaction with mercuric bromide to give the unstable benzylmercuric bromide, the constants of which were checked; and additional quantitative studies were called upon to eliminate the possible presence of any tolylmercuric bromides. These were obtained by conversion of the mercurial to the corresponding iodide and then reacting the halide with triethylamine to give the quaternary ammonium salt, $\llbracket(\text{C}_2\text{H}_5)_3\text{NCH}_2\text{C}_6\text{H}_5\rrbracket\text{I}$. By the resulting complete change of the iodide to titratable iodide ion it was proved conclusively that the benzyl compounds were present exclusively. Iodotoluenes, under these conditions, form no quaternary ammonium salts. Since hydrogen was the other product of thermal decomposition, equation (1) is probably correct. These particular findings speak well for the formation of bibenzyl on heating toluene to high temperatures in the absence of air.

In the course of the metalations of lateral hydrocarbons it was consistently noticed that metalation of the side chain was always enhanced by elevating the temperature of the reaction mixture. It is true that the temperatures used were low compared to those of Hein; but even this increase in temperature may cause a significant increase in dissociation or acidity of the hydrogen atoms

of the side chain over those of the nucleus. It should be noticed that in all cases where there was a possibility of either nuclear or lateral metalation, the metal entered the side chain at these higher temperatures. At low temperatures the nucleus was involved when the more reactive metalating agents such as n-butylsodium and ethylsodium were used.

In view of these findings, a possible explanation is offered for the discrepancy in the results obtained by Schorigin²⁰ on metalating toluene with ethylsodium from diethylmercury and with ethylsodium from diethylzinc. In the first case only phenylacetic acid was obtained while in the second case the phenylacetic acid was contaminated with p-toluic acid. Since the ethylsodium was prepared directly in the toluene, it is possible that the heat effect produced in the case of the mercurial was greater than in the case of the diethylzinc and any p-tolylsodium which was formed was immediately transformed to benzylsodium. Of course, there remains the possibility of a more pronounced catalytic effect of mercury on the migration of sodium, within the molecule, than is exerted by the displaced zinc.

The proposed hypothesis is still more strongly supported in view of the experiments which concern the migration of the alkali metal from the nucleus to the side chain

at elevated temperatures. The most striking case of migration is exhibited by p-tolylsodium. At room temperature a ligroin solution of p-chlorotoluene reacted with sodium to give p-tolylsodium exclusively, as was indicated by the formation of p-toluic acid subsequent to carbonation. However, on raising the temperature of the suspension of p-tolylsodium to the boiling point of ligroin (92°), benzylnsodium began to form immediately. The immediate formation of benzylnsodium was proved by carbonating an aliquot a few minutes after the application of heat, and by the fact that the color of the suspension changed from black to the typical brick-red of benzylnsodium. As a check, the p-tolylsodium was prepared from di-p-tolylmercury with similar strongly affirmative results. The yields of benzylnsodium obtained when toluene was used as a solvent were much higher, but the results are not as conclusive as those obtained when an inert solvent is used since the p-tolylsodium also has the possibility of metalating the toluene.

In order to determine the effect of the position of the alkali metal on migration, orienting experiments were run in which o- and m-tolylsodium were prepared in ligroin from the corresponding mercurials. These two nuclear alkali compounds undergo migration with increasing difficulty as is indicated by a decrease in yield of phenylacetic acid under corresponding conditions.

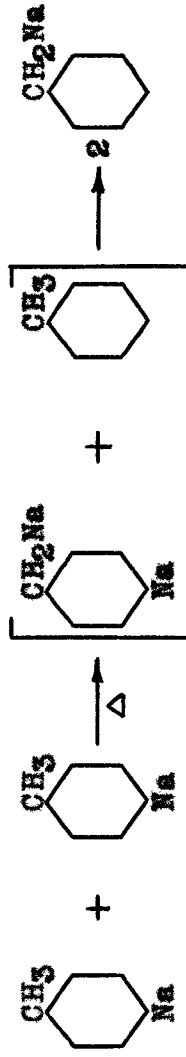
The kind of alkali metal involved has a very significant effect on whether migration will or will not occur. Potassium, like sodium, migrates in *p*-tolylpotassium to give benzylpotassium, although the yields are lower. However, in the case of *p*-tolyllithium, there is no rearrangement under similar conditions of temperature and solvent. The heating of *p*-tolyllithium to higher temperatures in mineral oil did not give very favorable results and to the present time no migration reactions of organolithium compounds have been observed.

Inasmuch as migration-metalations are centered about an allylic system in the case of *o*- and *p*-tolylsodium, there is some evidence which does not support an allylic rearrangement mechanism. For example, in *m*-tolylsodium the sodium and methyl groups are not part of an allylic system and still it rearranges to benzylsodium on heating. However, a different mechanism may be involved in the rearrangement of the meta compound since the yields of benzylsodium are low in comparison to those obtained from the ortho and para compounds.

The referee of a paper published recently by Gilman and co-workers¹⁸ suggested that the difficulties in attempting to apply the allylic rearrangement may be overcome by assuming the presence of a small amount of toluene resulting from slight hydrolysis of the benzylalkali

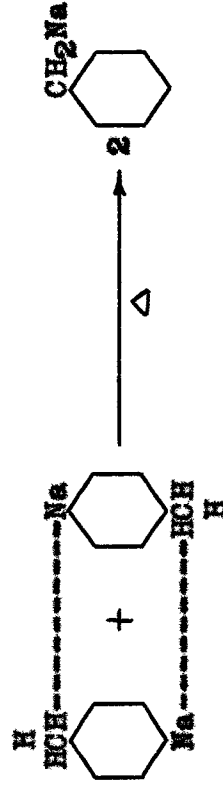
compound. The toluene would then be metalated by the tolylsodium with the formation of more toluene which would be metalated further. Only one molecule of toluene would be required to make this mechanism work. However, evidence against this suggestion is that the migration is very rapid and would undoubtedly be quite slow in this heterogeneous reaction mixture.

It may be possible that the following mechanism is involved although up to the present time the presence of the disodium intermediate has not been established:



In this mechanism it is necessary to assume that the p-sodiobenzylsodium is very reactive and metalates the toluene instantaneously.

Since the tolylsodium molecules occur in clusters, the mechanism which is favored is one of strict auto-metalation involving the simultaneous exchange of two atoms of sodium for two atoms of hydrogen between two molecules of the tolylsodium compound:



This change should be very rapid and controlled by the increased lability of the methyl hydrogen atoms brought about by elevated temperatures.

The lateral metalation of aromatic hydrocarbons is not a general reaction and this may be seen from the following results. *o*-Methylnaphthalene, the closely related isomer of *β*-methylnaphthalene, is not metalated by either phenylsodium or the "chlorobenzene-potassium system". *β*-Methylnaphthalene was metalated laterally to an extent of 4% by phenylsodium while *n*-butylsodium gave a 30% yield of metalation product. *o*-Methylnaphthalene, on the other hand, was metalated by *n*-butylsodium to give a 12% yield of acidic product, subsequent to carbonation, which was undoubtedly a mixture of nuclear and lateral acids. *Bi-o*-tolyl could not be metalated by *n*-butylsodium.

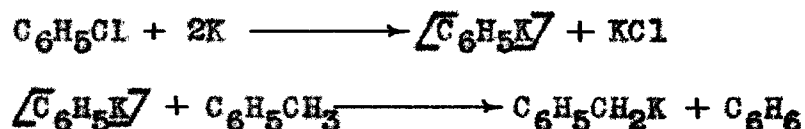
Some studies have been carried out on the metalation of side chains which contain more than one carbon atom. The results of these experiments show that metalation, when it occurs, concerns the alpha carbon atom and the yield of product is very poor. Scherigin²¹ found that ethylsodium metalated ethylbenzene to give a 1% yield of hydrotropic acid; diphenylmethane gave a 0.9% yield of diphenylacetic acid; and *p*-cymene gave a 2.2% yield of *p*-homocumic acid. We have made attempts to metalate ethylbenzene and *n*-propylbenzene with phenylsodium but all the

results were negative. Dr. R. V. Young¹⁸ has metalated isopropylbenzene with ethylsodium to obtain a 41% yield of phenylisopropylsodium.

The "chlorobenzene-potassium system," that was mentioned above, is of a very interesting nature and merits a discussion. Phenylpotassium has never been prepared from chlorobenzene and potassium, in benzene solution, because a Wurtz reaction occurs with the formation of biphenyl. However, it was found that this coupling reaction could be interrupted at the intermediate organometallic stage by a proper choice of solvent. This is illustrated very strikingly in the case of the preparation of benzylpotassium and 3,5-dimethylbenzylpotassium wherein the solvents are toluene and mesitylene, respectively. The mechanism of the reaction depends upon the establishment of the "chlorobenzene-potassium system". In the case of the formation of benzylpotassium from potassium and chlorobenzene in toluene solution, the phenylpotassium which forms for a fleeting instant is trapped by the toluene and thus kept from reacting with excess chlorobenzene. The benzylpotassium which results is less reactive towards chlorobenzene than is phenylpotassium and the Wurtz reaction is interrupted at this stage. Even at low temperatures and in various solvents, the elusive phenylpotassium could never be isolated. For this reason the metalation of

compounds by a mixture of chlorobenzene and potassium, for want of a more exacting term, is called the metalation by the "chlorobenzene-potassium system".

The reaction is best illustrated by writing the equations in the following manner:



The old question of solvent effects is again brought up as a consequence of our experiments. Unfortunately the results obtained in the control experiments which were performed do not clarify this problem as far as generalities are concerned. Diethyl ether cannot be used as a reaction medium in these reactions of the benzylalkali compounds, with the exception of benzyl lithium, as it is immediately destroyed. The migration of sodium in *p*-tolylsodium was studied in various solvents (See page 70) and the yields were found to vary from fifty to sixty per cent. Preparation of many of the organoalkali compounds in ligroin is accelerated by refluxing the reaction mixture for several minutes and then heating gently for several hours. This method was used to bring about the rearrangement of *o*-, *m*-, and *p*-tolylsodium, prepared from the corresponding mercurials. A closed tube experiment still in progress, in which an attempt is being made to

determine whether rearrangement of p-tolylsodium takes place at room temperature, required many months before a noticeable reaction occurred. Paraffin oil, although it is a means of obtaining high temperatures, did not give satisfactory results in an attempt to rearrange p-tolyl-lithium above 250°.

Phenylsodium, a compound that is inexpensive and easily prepared, was used as a metalating agent in many of the studies described. However, a limitation must be placed on its use inasmuch as the reactions in which it is employed must be metathetically complete, otherwise the desired acid, obtained as a result of the metalation, will be contaminated with benzoic acid. It was found that many times the last traces of the phenylsodium may be removed by prolonged heating since this compound appears to be destroyed, to a small degree, by this treatment.

The preparation of benzoic acid from chlorobenzene and sodium in toluene suspension, subsequent to carbonation, definitely indicated that the first step in the new method for preparing benzylsodium was the formation of phenylsodium. This fact, incidentally, helps to validate our assumption that phenylpotassium is formed as an intermediate in the preparation of benzylpotassium. No p-toluic acid was ever isolated in these cases.

On heating a toluene suspension of phenylsodium it was observed that the product after rapid carbonation was solely phenylacetic acid. In order to check the possibility of an equilibrium between the benzyl- and phenylsodiums an ordinary run of phenylsodium was made in toluene and on carbonating an aliquot of the suspension only benzoic acid was found. The toluene was replaced by a like quantity of benzene and after allowing sufficient time for a possible equilibrium to occur, the mixture was carbonated. No benzoic acid was isolated and this is in accord with the prediction that may be drawn from the electronegativity series of Kharasch.⁵³ However, Bachmann and Clarke⁵² obtained a result which questions the validity of the Kharasch series as a tool for predicting the relative acidities of the hydrogen atom by metalation reactions inasmuch as they obtained large amounts of phenylsodium when they reacted di-*p*-tolylmercury with sodium in benzene solution. The reaction was allowed to proceed for a period of thirty days and the results obtained indicate that the *p*-tolylsodium must have metalated the benzene; this is contrary to any prediction resulting from the Kharasch electronegativity series.

n-Butylsodium, which is expensive and somewhat difficult to obtain, is undoubtedly a superior metalating agent in comparison with phenylsodium. This fact is illustrated

in the metalation of β -methylnaphthalene and t-butylbenzene with n-butylsodium and also phenylsodium; 30% of β -naphthylacetic acid was obtained with n-butylsodium while phenylsodium gave only a 4% yield; n-butylsodium gave an 11% yield of p-t-butylbenzoic acid while phenylsodium gave no acid. Experiments now in progress indicate that n-amylsodium is approximately as good as n-butylsodium for metalating β -methylnaphthalene, with the added advantage of being inexpensive and easy to prepare.

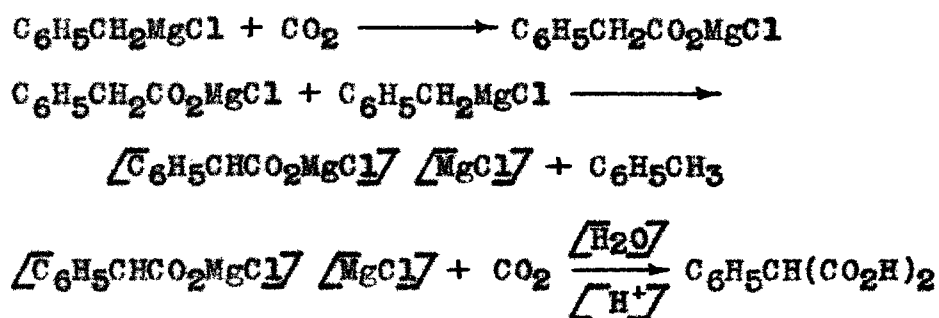
As a consequence of the negative results obtained in the attempts to metalate α -methylnaphthalene, several studies were suggested in order to determine the effect of nuclear unsaturation on lateral metalation. Cyclohexane, methylcyclohexane, 1-methylcyclohexene and 3-methylcyclohexene were not metalated by either phenylsodium or n-butylsodium. Since the methylcyclohexenes did not show the slightest tendency to be metalated, the studies were suspended.

n-Butyllithium is one of the few known organolithium compounds capable of successfully bringing about a lateral metalation. In our studies we found that toluene was metalated to an extent of 0.22% and Gilman and Webb⁶¹ metalated methyl phenyl sulfide, laterally, to an extent of 62%. The very closely related oxygen analog, anisole, undergoes metalation only in the ortho position. It would

be very interesting to know whether a migration of lithium would occur from the nucleus to the side chain of a compound such as *p*-methylmercaptophenyllithium. If this did occur, it would be the first known case of a migration of the lithium atom from the nucleus to the side chain of an organolithium compound. However, the apparent unpredictable nature of lithium compounds in organometallic chemistry may be a carry-over from inorganic chemistry and rearrangements may never occur.

In view of the uncertainty involved in the mechanism of formation of substituted malonic acids on carbonation of benzylsodium and alkylsodium compounds, some studies were undertaken to clarify this problem.

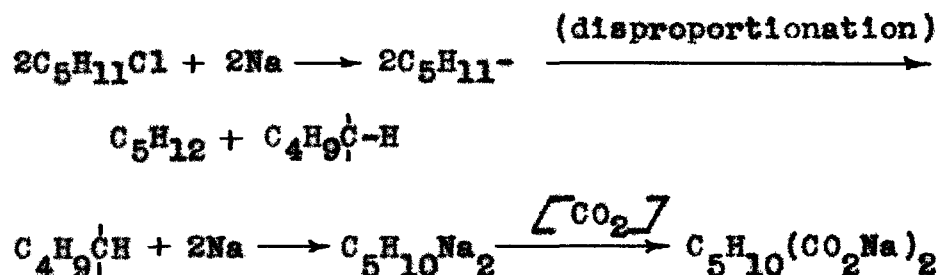
The first formation of a substituted malonic acid was observed by Ivanoff and Spassoff⁹⁴ when they obtained phenylmalonic acid on carbonating benzylmagnesium chloride with gaseous carbon dioxide. They proposed the following mechanism for its formation:



94. Ivanoff and Spassoff, Bull. soc. chim., 49, 19 (1931).

Unfortunately Morton and co-workers²⁷ overlooked the work of Ivanoff and Spassoff, and in their work on the formation of phenylmalonic acid by carbonating benzylsodium they claimed priority of this reaction by saying that, "the formation of phenylmalonic acid by this method, the principal product in a toluene medium, has never to our knowledge been recorded before".

The results of the carbonation studies that were undertaken question the validity of the amylienedisodium mechanism of Morton.⁹⁵ After many extensive studies on the effect of time, temperature, solvent and rate of stirring were carried out, the mechanism which he assumed to be the correct one was the formation of amylienedisodium by the following free radical mechanism:



He ruled out the earlier proposed mechanism in which it was assumed that the amylienedisodium was a result of metalation,



by subjecting the suspension of the n-amylsodium to heat.⁹⁶

95. Morton and Hechenbleikner, J. Am. Chem. Soc., 58, 1697 (1936).

96. Morton and Hechenbleikner, ibid., 58, 1024 (1936).

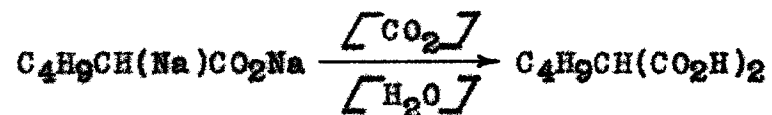
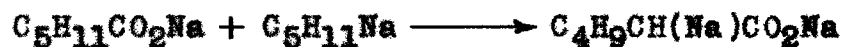
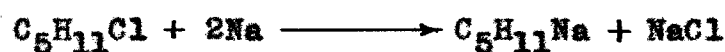
The yield of caproic acid decreased with continued heating while the amount of n-butylmalonic acid which was isolated did not change. If this mechanism had been the correct one, the yield of n-butylmalonic acid should have increased with the decomposition of the n-amylsodium.

The mechanism of metalation of the sodium caproate by n-amylsodium was eliminated when the yields of n-butylmalonic acid were not increased on adding determined quantities of n-caproic acid to the n-amylsodium.⁹⁷ On the other hand, when the n-caproic acid was added to phenylsodium it was found that a metalation took place with the formation of sodium sodiocaproate. n-Amylsodium appears to be a more powerful metalating agent than phenylsodium and for this reason some attempt must be made to explain this inconsistency in metalating effects. Since the metalation reaction is one that occurs between two salts, physical factors may explain this discrepancy. It is suggested that this particular metalation is a surface phenomenon and its success depends upon the particle size of the sodium caproate formed prior to its metalation by the organometallic compound. Phenylsodium may react with n-caproic acid to form sodium caproate particles of a molecular size while aggregates may occur in the case of n-amylsodium causing a very difficult reaction. It seems

97. Morton, Falwell and Palmer, Ibid., 60, 1428 (1938).

probable that a reaction does occur in the latter case, but to such a slight extent that the increase in butylmalonic acid which forms is not determinable by the methods employed in this study.

Assuming that physical factors play a part in the success of the reaction, the mechanism which appears to be the correct one according to the results of our studies is the one analogous to that of Ivanoff and Spassoff:



The experiments in which parallel runs of n-amylsodium were carbonated at different rates are offered as convincing evidence for this mechanism. On carbonating the organosodium compound with gaseous carbon dioxide at a very slow rate, very significant quantities of n-butylmalonic as well as n-caproic acid were formed. This condition is ideal for the formation of the malonic acid since there is always an excess of organometallic present throughout the carbonation. On the other hand, when the n-amylsodium was rapidly poured on an excess of crushed solid carbon dioxide only a very insignificant quantity of n-butylmalonic acid was formed.

This result is in perfect accord with the prediction made from the favored mechanism.

In a private communication from Professor A. A. Morton, who acknowledged our results as very significant, it was suggested that these experiments be rerun in the same medium, low-boiling petroleum ether, which he used. Heretofore we employed ligroin but the results remained unchanged when the suggested solvent was used.

The results obtained by the rapid and slow carbonations of benzylnaodium were even better defined than in the case of n-amylsodium as no phenylmalonic acid was obtained on rapid carbonation.

The tabulated results obtained in studying the effects of the rate of carbonation may be found on pages 79 to 82.

The formation of substituted malonic acids apparently is general, as claimed by Morton, but only under conditions of gaseous carbonation. That the yield of malonic acid is dependent upon the rate of admission of gaseous carbon dioxide was shown by carbonating a run of n-amylsodium with a very rapid stream of the gas and obtaining a much decreased quantity of n-butylmalonic acid. It may be mentioned that after rapidly carbonating a run of n-amylsodium, with solid carbon dioxide, which had been allowed to stir at room temperature for sixty-two hours, no n-butylmalonic acid could be obtained. If we eliminate the

unlikely possibility that amylienedisodium does not react with solid carbon dioxide, the above experiment apparently indicates that there is no equilibrium between amylienedisodium and amylnsodium.

Benzylpotassium and 3,5-dimethylbenzylpotassium both gave significant quantities of phenylmalonic and 3,5-dimethylphenylmalonic acid when carbonated by a slow stream of gaseous carbon dioxide.¹⁸

Several experiments other than those involving rates of carbonation have been carried out and indicate that the reactions of the lateral organoalkali compounds are similar to those of most organometallic compounds. The carbonation reaction, which is somewhat of an exception, is normal when performed rapidly. Reaction with the carbonyl group proceeds very smoothly as is indicated by the preparation of diphenylbenzylcarbinol,¹⁸ in good yields, from benzylpotassium and benzophenone. Gaseous formaldehyde as well as paraformaldehyde did not give satisfactory yields of β -phenylethyl alcohol with benzylsodium. o-Tolylcarbinol was shown to be absent since oxidation of the products gave only benzoic and no phthalic acid.

Since Schlenk³⁸ did not mention the yield of phenylacetic acid obtained on carbonating benzylsodium prepared from dibenzylmercury and sodium in ligroin suspension, an orienting experiment was performed in which a 62% yield of

phenylacetic acid was obtained using his method. The fact that Kirby⁶⁶ was unable to isolate any of this acid from the experiments in which he exchanged the ligroin of a benzylnsodium suspension for diethyl ether indicates that the large quantities of benzylnsodium which were present at the beginning were rapidly destroyed by this solvent.

Dr. T. H. Cook⁸⁰ found that benzylnsodium was an excellent metalating agent in the case of dibenzofuran, inasmuch as he was able to isolate a 78% yield of 4-carboxydibenzofuran. Dr. O. Baine,⁹⁸ in some extensive metalation studies, independently obtained an 80% yield of 4-carboxydibenzofuran when he used benzylnsodium as a metalating agent. He also found that benzylpotassium does not metalate dibenzofuran, even when refluxed in toluene for periods of 24 and 48 hours. The recovery of phenylacetic acid in each of these cases was 70 to 80% indicating that benzylpotassium is thermally stable. These negative metalation results with benzylpotassium are very surprising and as yet are not explainable.

An attempt to react benzyl chloride and also cyclohexyl chloride with sodium to give benzylnsodium and cyclohexylsodium, respectively, terminated in negative results.

The fact that β -naphthylacetic acid cannot be obtained by convenient methods led to the investigation of the lateral

98. Dr. O. Baine, Unpublished results.

metalation of β -methylnaphthalene as a possible source of this compound. This acid, which is used in botanical research as a synthetic plant hormone, was obtained by carbonating β -naphthylmethylsodium prepared from β -methylnaphthalene and n-butylsodium. The yield of acid was 30%, but the method of preparation is not very economical although quite convenient. Phenylsodium metalated the β -methylnaphthalene to an extent of 4.3% and this result was checked by Mr. R. W. Leeper.

The preparation of benzyl lithium by a direct method was investigated with only unsatisfactory results being obtained. Phenyl lithium could not be induced to metalate toluene, no matter how the conditions were altered. Benzyl chloride would not react with lithium in toluene solution; di-p-tolylmercury was not cleaved by sodium in ligroin solution; and n-butyl lithium did not metalate toluene when the diethyl ether, in which it was prepared, was completely replaced by toluene. n-Butyl lithium prepared in toluene metalated this hydrocarbon to an extent of 0.22%, a yield which eliminates this method as far as preparative value is concerned.

The increasing importance of the interconversion reaction in synthesis suggested the possibility of preparing benzyl lithium by this method. Benzyl chloride on reaction with n-butyl lithium gave a rapid coupling reaction and with

phenylethynyllithium, there was no reaction. Benzylsodium in ether solution did not react with anhydrous lithium bromide.⁹⁹

Attempted interconversion reactions between n-butylsodium and chlorobenzene, p-chlorotoluene, and α -chloronaphthalene all ended in negative results.

Halogen-metal interconversion reactions up to the present time have been shown to occur to a predictable extent only with aryl halides⁴⁰ and alkyllithium compounds.

Extensive studies have been carried out on the interconversion of α -bromonaphthalene and n-butyllithium.¹⁰⁰ In line with this work, an interconversion was shown to occur between α -bromonaphthalene and n-butylsodium to give a 26% yield of α -naphthoic acid subsequent to carbonation. This is apparently the first halogen-metal interconversion in which the alkali metal is other than lithium. Gilman and co-workers⁴⁰ have further shown the general nature of this type of interconversion reaction by obtaining an interconversion of n-butyllithium with aryl chlorides and iodides as well as the bromides. Wittig¹⁰¹ has indicated that an interconversion occurs when o-chloro- and o-fluoroanisole are treated with phenyllithium.

An investigation of the effect of steric factors on halogen-metal interconversions of some sterically hindered

99. Kindly provided by Mr. R. G. Jones.
100. Gilman and Moore, ibid., 62, 1843 (1940).
101. Wittig, Angew. Chem., 53, 245 (1940).

bromo-compounds gave results of a very significant nature as indicated in the following table.

TABLE XXII

Steric Effects in Halogen-Metal Interconversions*

<u>Compound</u>	<u>Time required to get the maximum yield</u>	<u>Per cent inter-conversion to corresponding nuclear acid</u>
2,4,6-Trimethylbromobenzene	60 minutes	40
2,4,5-Trimethylbromobenzene	15 "	63
p-Bromo-t-butylbenzene	30 "	86

*n-Butyllithium used in all cases.

The discrepancy in the time required to obtain the maximum yield of p-t-butylbenzoic acid may not have any significance since no aliquots were taken in this experiment. These results indicate that the interconversion reaction occurs to a greater extent on increased exposure of the halogen atom within the molecule.

The possibility of the allylic rearrangement of benzylsodium was checked using gaseous formaldehyde, paraformaldehyde and acetic anhydride. In each of these cases only benzoic acid was obtained on oxidation of the reaction product indicating the absence of ortho rearrangement products.

With respect to the results obtained in the migration studies involving the shift of metal from the nucleus to the

side chain on heating, it was thought that the allylic rearrangement of benzylmagnesium chloride would be hindered by such treatment. In contradiction to the prediction, it was found that the allylic rearrangement was enhanced by heating, occurring to an extent of 10.5% at 15° and 18% at 90°.

V. SUMMARY

The preparation and reactions of lateral organoalkali compounds have been reviewed.

The selective metalation of the side chain in lateral aryl hydrocarbons has been shown to occur to a practical extent.

Benzylpotassium and 3,5-dimethylbenzylpotassium have been prepared for the first time with the aid of a hypothetical "chlorobenzene-potassium" system.

Sodium as well as potassium atoms were found to migrate from the nucleus to the side chain in compounds such as *p*-tolylsodium and *p*-tolylpotassium. Several mechanisms have been suggested for this rearrangement.

The effect of the rate of carbonation of lateral and alkyl organosodium and -potassium compounds has been investigated. Substituted malonic acid formation was favored by slow gaseous carbonation.

The results of some halogen-metal interconversion reactions indicated that steric factors affect the rate of interconversion.

A sodium-bromine interconversion has been reported.

An increased temperature was shown to enhance the allylic rearrangement of formaldehyde with benzylmagnesium chloride.