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Long-chained organometallic compounds

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LONG-CHAINED ORGANOMETALLIC COMPOUNDS

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by

Robert Nelson Meals

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I. INTRODUCTION

The study of long-chained organometallic compounds is of interest for several reasons. The compounds themselves may prove useful as lipophilic chemotherapeuticals, or they may have other uses from which their lower homologs are barred by reason of their volatility, solubility behavior, toxicity, or inflammability. They may serve as tools for introducing long chains into organic compounds. From the standpoint of pure organic chemistry, they are a contribution to our knowledge of homology.

Relatively few long-chained organometallic compounds have been prepared. Aside from a few lithium, sodium, magnesium, and mercury derivatives, the subject has received very little consideration. The investigations described in this thesis are concerned chiefly with the higher alkyl compounds, from dodecyl to octadecyl, of the metals of the first, second, fourth, and fifth groups of the periodic table.

II. HISTORICAL

A. Compounds of the first periodic group.

The preparation of dodecyllithium in diethyl ether from n-dodecyl bromide and lithium has been described (1). Dodecyl bromide was used rather than dodecyl chloride, although Ziegler and Colonius (2) had obtained considerably better results with n-butyl chloride than with n-butyl bromide. The yield of dodecyllithium was reported to be 38.5% when the bromide was added slowly, or 30.2% when it was added all at once. It has been found, however, that the simple acid-base titration method (3) used in this study (1) is not applicable to organolithium compounds (4) and especially to organolithium compounds prepared in ether (5). The yield of dodecyllithium was therefore probably somewhat lower than 30%. More recently Hoyt and Gilman (6) have reported the preparation of n-dodecyllithium and n-tetradecyllithium, but the yields were not stated.

1. Gilman, Zoellner, and Selby, J. Am. Chem. Soc., 55, 1252 (1933).

2. Ziegler and Colonius, Ann., 479, 135 (1930).

3. Gilman, Wilkinson, Fishel, and Meyers, J. Am. Chem. Soc., 45, 150 (1923).

4. A. H. Haubein, unpublished work.

5. Ziegler, Crössmann, Kleiner, and Schäfer, Ann., 473, 1 (1929).

6. Hoyt and Gilman, Proc. Iowa Acad. Sci., 45, 133 (1938).

Pontz (7) prepared n-octadecyllithium from the bromide. The yield was 41% by simple titration.

A study of the rate of hydrogenation of lithium compounds in benzene solution showed that in this reaction the reactivity of the lithium alkyls decreased as the length of the chain increased. While methyllithium reacted in 38.5 hours, n-heptyllithium required 66 hours, and n-dodecyllithium required 91 hours. The method of preparation and the yield of the dodecyllithium were not reported (8). It is not to be concluded, however, that long-chained lithium compounds are markedly less reactive than the shorter homologs, for dodecyllithium reacted completely with excess benzonitrile within four minutes, the same length of time that was observed for n-butyllithium (9).

Although long-chained alkyl halides have been reacted with sodium in a number of cases, in very few have there been any attempts to show the presence of an organosodium compound. Gascard (10) showed that pentadecyl iodide when refluxed in xylene with sodium gave triacontane. Octadecyl iodide similarly yielded hexatriacontane. The yields were not stated, nor were the other products investigated. Hexadecyl iodide

7. D. F. Pontz, unpublished work.

8. Gilman, Jacoby, and Ludeman, J. Am. Chem. Soc., 60, 2336 (1938).

9. Gilman and Kirby, ibid., 55, 1265 (1933).

10. Gascard, Compt. rend., 153, 1484 (1911).

when heated with sodium, with or without ether, gave dotria-
contane (11). It is not likely that organosodium compounds
could have been shown to have been formed in these reactions,
for the alkyl iodides are too reactive in the coupling
reaction

$$RI + RNa \longrightarrow RR + NaI$$

to be of use in the preparation of organoalkali compounds (2).

Hexadecyl bromide, which might be expected to form small
amounts of hexadecylsodium, gave with sodium and ether a light
blue powder and an 88% yield of dotriacontane (12). The blue
substance was found to be sodium bromide. No attempt was made
to establish the presence of an organosodium compound.

Schlenk and Holtz (13) believed that long-chained organo-
sodium compounds might be soluble in hydrocarbon solvents.
They therefore prepared n-octylsodium, which was the longest
homolog available to them since they used the bismercurials
as starting materials, and dioctylmercury was then the highest
known compound of this type (14). They found that octylsodium
was insoluble in petroleum ether.

Hexadecyl chloride reacted with sodium sand in ligroin at
30°, under pressure of carbon dioxide, to give a 9% yield of

11. Meyer and Soyka, Monatsh., 34, 1159 (1913).

12. Schlubach and Goes, Ber., 55, 2889 (1922).

13. Schlenk and Holtz, ibid., 50, 262 (1917).

14. Eichler, ibid., 12, 1879 (1879).

margaric acid and a 30% yield of pentadecylmalonic acid (15).
Under similar conditions the total yields of acids with other
chlorides were: n-butyl 25%, n-amyl 63%, and n-hexyl 45%.
The yield of amylsodium has since been increased as high as
95% (16), so it is to be expected that the yield of hexadecyl-
sodium might be increased beyond 39% under the proper conditions.

Amylpotassium was prepared in 1.9% yield from n-amyl
chloride and potassium sand in ligroin. Amyllithium prepared
under similar conditions yielded only 4.6% of acids on car-
bonation (17). Since organolithium compounds give ketones as
well as acids on carbonation the yield of RLi was greater than
4.6% (18).

B. Compounds of the second periodic group.

Dibutylberyllium is apparently the highest beryllium
dialkyl to have been prepared (19). It was made from the
Grignard reagent and beryllium chloride.

Long-chained organomagnesium compounds have frequently
been used to introduce the higher alkyl groups into organic
and organometallic compounds. Oskerko (20) observed that

15. Morton, LeFevre, and Hechenbleikner, J. Am. Chem. Soc., 58,
    754 (1936).

16. Morton and Richardson, ibid., 62, 123 (1940).

17. Morton and Hechenbleikner, ibid., 58, 1697 (1936).

18. Gilman and van Ess, ibid., 55, 1258 (1933).

19. Gilman and Schulze, J. Chem. Soc., 2663 (1927).

20. Oskerko, J. Russ. Phys.-Chem. Soc., 46, 411, 416 (1914)
    /Chem. Zentr., II, 1264-5 (1914)/.

n-octadecyl bromide reacted with magnesium in ether to yield octadecylmagnesium bromide; treatment of this product with carbon dioxide gave the expected (21) nonadecanoic acid. Hexatriacontane was obtained as a by-product. No mention was made of octadecane or octadecene among the products; the reaction was believed to be simply

$$2 C_nH_{2n+1}X + Mg \longrightarrow (C_nH_{2n+1})_2 + MgX_2$$
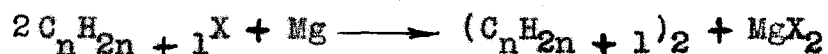
Tridecyl iodide, tetradecyl iodide, pentadecyl iodide, hexadecyl iodide, and octadecyl iodide were observed to give the coupling products, hexacosane, octacosane, triacontane, dotriacontane, tetratriacontane, and hexatriacontane, when treated with magnesium in ether. The yield of the dotriacontane was 70-80%; the other yields were not stated (22).

Methylmagnesium iodide reacted with n-hexadecyl iodide to give, as one of the products, dotriacontane (23). This was explained by assuming the formation of free radicals:

$$RMgX + R'X' \longrightarrow R + R' + MgXX'$$

Methane, ethane, hexadecane, hexadecene, and heptadecane were also found. Another possible explanation of this interesting reaction involves halogen-metal interconversion (24),

21. Houben and Kesselkaul, Ber., 35, 2519 (1902).

22. Levene, West, and van der Scheer, J. Biol. Chem., 20, 521 (1915).

23. Späth, Monatsh., 34, 1965 (1913).

24. Gilman, Langham, and Moore, J. Am. Chem. Soc., 62, 2327 (1940).

followed by coupling:

$$CH_3MgI + C_{16}H_{33}I \longrightarrow CH_3I + C_{16}H_{33}MgI$$

$$C_{16}H_{33}MgI + C_{16}H_{33}I \longrightarrow C_{32}H_{66} + MgI_2$$
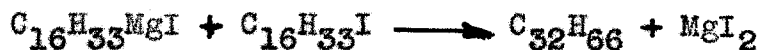
It would be of interest to see whether margaric acid could be obtained on carbonation of such a reaction mixture.

Ruttan (25) obtained margaric acid by carbonation of hexadecylmagnesium bromide or iodide. He reported dotriacontane as a by-product when the iodide was used; it is also formed when the bromide is used but in lesser amounts.

Hill (26) used n-nonylmagnesium bromide and n-dodecylmagnesium bromide with mercuric bromide to prepare the alkylmercuric bromides. Slotta and Jacobi (27) made n-hexadecylmercuric bromide from hexadecylmagnesium bromide, in 90% yield.

Houben, Boedler, and Fischer (28) studied the preparation of long-chained Grignard reagents. They found that n-hexadecyl chloride, though it reacted slowly with magnesium, gave excellent yields (96%) of hexadecylmagnesium chloride. Hexadecyl bromide gave only 81.4% of hexadecylmagnesium bromide, while the iodide gave 79.7%.

Long-chained alkyl iodides can be used to prepare the

25. Ruttan, Eighth International Congress of Applied Chemistry, 25, 431 (1912) /Chem. Zentr., I, 2108 (1913)/.

26. Hill, J. Am. Chem. Soc., 50, 167 (1928).

27. Slotta and Jacobi, J. prakt. Chem., 120, 249 (1929).

28. Houben, Boedler, and Fischer, Ber., 69, 1766 (1936).

Grignard reagents, but are inferior to the chlorides or bromides because of the relatively large amount of coupling that takes place. In fact, Oldham and Ubbelohde (29) used dodecyl, tetradecyl, hexadecyl, and octadecyl iodides with magnesium and iodine to prepare tetracosane, octacosane, dotriacontane, and hexatriacontane. The yields of Grignard reagents were 64% or more, if no iodine was added to the mixture. With five additions of iodine and magnesium, about 65% of coupling products were obtained.

Gilman and McCracken (30) obtained an average yield of 73.7% of Grignard reagent from n-dodecyl bromide. Gilman, Zoellner, and Selby (1) reported an 85.3% yield of dodecylmagnesium bromide, and mentioned that the decrease on rapid addition of dodecyl bromide to magnesium was 11%.

Strating and Backer (31) prepared n-dodecylmagnesium bromide and reacted it with ethyl acetate in their synthesis of methyldidodecylmethane. They obtained a 70% yield of Grignard reagent. Backer and Haack (32) made the Grignard reagent from 41.6 grams (0.15 mole) of n-tetradecyl bromide. After this had been allowed to react with 8.3 grams (0.05 mole) of 2,3-dimethoxybenzaldehyde and then was hydrolyzed, there were obtained 13 grams (0.076 mole) of n-tetradecane,

29. Oldham and Ubbelohde, J. Chem. Soc., 201 (1938).

30. Gilman and McCracken, J. Am. Chem. Soc., 45, 2462 (1923).

31. Strating and Backer, Rec. trav. chim., 55, 903 (1936).

32. Backer and Haack, ibid., 57, 225 (1938).

3 grams (0.009 mole) of octacosane, and some tetradecyl alcohol, as well as 2 grams of the desired 2,3-dimethoxypentadecenylbenzene. Apparently the tetradecane fraction was not examined for unsaturated hydrocarbons.

Oldham and Ubbelohde (29) reported a 91.5% yield of Grignard reagent from n-dodecyl chloride and magnesium. This is considerably higher than the yield usually obtained from dodecyl bromide, and confirms the observations of Houben, Boedler, and Fischer (28).

Lüttringhans, Sääf, and Hauschild (33) used dodecyl-magnesium bromide to cleave allyl phenyl ether. The Grignard reagent prepared from 32 grams (0.125 mole) of dodecyl bromide was heated with 13.4 grams of allyl phenyl ether, and held at 75° for six hours. There were obtained a 71% yield of phenol, 10.5 grams of a mixture of dodecane and unreacted allyl phenyl ether, 3.2 grams of tetracosane (0.0094 mole), and 9.0 grams (43% of theoretical based on the ether used) of n-pentadecene-1. Similar results were obtained with n-butyl and phenyl Grignard reagents, so the behavior did not change with lengthening the carbon chain.

John, Günther, and Schmeil (34) prepared n-dodecyl-magnesium bromide and reacted it with dihydrocoumarin to obtain the 2,2-didodecyl derivative:

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33. Lüttringhaus, Sääf, and Hauschild, Ber., 71, 1673 (1938).

34. John, Günther, and Schmeil, Ber., 71, 2637 (1938).
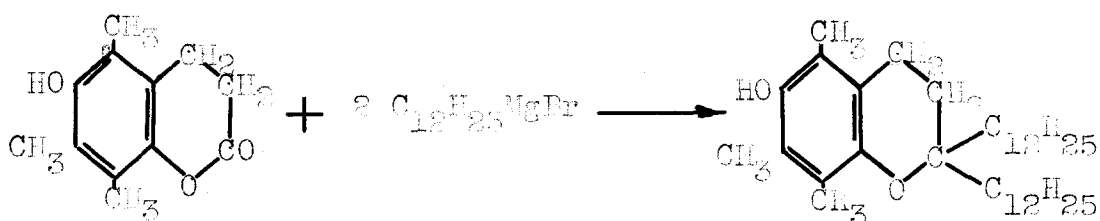
A mixture of dodecylmagnesium bromide and methylmagnesium iodide reacted with dihydrocoumarin to give a mixture of the three 2,2-dialkyl products. The mixed dialkyl
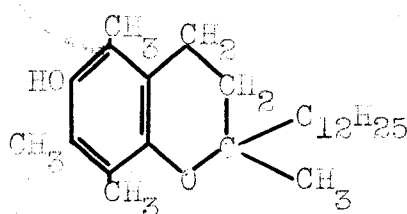
was obtained in 10-15% yield. The behavior of the long-chained Grignard reagent was again entirely normal.

Gilman and Kirby (9) reacted n-dodecyllithium with benzonitrile, and n-dodecylmagnesium bromide with benzonitrile, under the same conditions (0.03 mole of organometallic compound with 0.033 mole of C_6H_5CN in a total ether volume of 220 cc.). The lithium compound reacted within four minutes, while the Grignard reagent was not completely reacted after three hours. The authors concluded that the length of the

carbon chain is without essential influence on the relative
rates of reaction of the two types (lithium and magnesium) of
compounds. Gilman, St. John, St. John, and Lichtenwalter (35)
found that n-dodecylmagnesium bromide reacted completely with
benzonitrile in 1.47 hours. The conditions of the experiment
were not the same as those in the similar experiment of
Gilman and Kirby (34); here 0.025 mole of RMgBr and 0.03 mole
of benzonitrile were used in a total volume of 37.5 cc. The
time of reaction was shorter than that observed with any of
the other n-alkylmagnesium halides (with the exception of the
ethyl) used in this series of experiments. It is evident that
in this reaction the lengthening of the alkyl chain does not
decrease the reactivity of the Grignard reagent. The results
of Gilman, Jacoby, and Ludeman (8) which showed dodecyl-
lithium to be less reactive than methyllithium or heptyl-
lithium, merely illustrate, perhaps, that the "relative reac-
tivity" depends to a large extent on the reaction used.

Qualitatively, these experiments indicate that there is
no great difference in reactivity among the alkyl Grignard
reagents of different chain lengths, and it has been found
that the long-chained reagents can be used successfully in
any reaction in which the shorter homologs are known to take
part. For example, Goebel and Marvel (36) found that

35. Gilman, St. John, St. John, and Lichtenwalter, Rec. trav.
chim., 55, 577 (1936).

36. Goebel and Marvel, J. Am. Chem. Soc., 55, 1693 (1933).

n-hexadecylmagnesium bromide can be oxidized readily at $0°$ to give good yields (59%) of hexadecyl alcohol.

No attempts have been made to make long-chained calcium, strontium, or barium compounds. Schulze (37) reacted n-octyl iodide with calcium in ether, with iodine as a catalyst, and obtained a positive color test (38), indicating the presence of octylcalcium iodide, and a 17.8% yield of hexadecane. Ethyl iodide and iodobenzene did not react with strontium metal under various conditions of time and temperature, and in the presence of iodine or mercuric chloride and iodine. Metallic barium proved to be equally inert (37). A previous report claimed the preparation of ethylbarium iodide from ethyl iodide and barium (39), but according to Schulze this "barium" was later found to contain calcium, chiefly, and only a trace of barium. There are two rather puzzling features to the work done to date on the organometallic compounds of these three elements: the inertness of strontium and barium in comparison with calcium, and the inactivity of chlorides and bromides toward calcium (40).

Diisoamylzinc (41) and diisoamylcadmium (42) have been

37. Schulze, Iowa State College J. Sci., 8, 225 (1933).

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

39. Gilman and Schulze, Bull. soc. chim., 41, 1333 (1927).

40. Glacet, ibid., 5, 895 (1938).

41. Krause and Fromm, Ber., 59, 931 (1926).

42. Krause, ibid., 50, 1813 (1917).

prepared from the halides and the Grignard reagents. There is no reason to believe that higher homologs could not be prepared, although their isolation might present a problem.

Eichler (14) used n-octyl iodide with sodium amalgam and ethyl acetate, the method of Frankland and Duppa (43), to prepare dioctylmercury, which was described as a colorless, oily liquid of faint odor. At 200° it decomposed into hexadecane and mercury.

Pontz (7) prepared di-n-octadecylmercury from "octadecylmercuric bromide" and octadecylmagnesium bromide. Although the compound so obtained had the same properties as the dioctadecylmercury described in the experimental portion of this thesis, Pontz was unable to analyze it correctly for mercury.

The acetylide, dinonadecinylmercury, was prepared from 1-nonadecyne (44). Dipentadecinylmercury was obtained from 1-pentadecyne (45). These compounds were used as derivatives of the hydrocarbons.

Hill (26) prepared n-nonylmercuric bromide and n-dodecylmercuric bromide from mercuric bromide and the alkylmagnesium bromides. Vaughn, Spahr, and Nieuwland (46) prepared

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43. Frankland and Duppa, Ann., 130, 104 (1864).

44. Coffman, Tsao, Schniepp, and Marvel, J. Am. Chem. Soc., 55, 3792 (1933).

45. Ryden, Glavis, and Marvel, ibid., 59, 1014 (1937).

46. Vaughn, Spahr, and Nieuwland, ibid., 55, 4206 (1933).

n-decylmercuric bromide from decylmagnesium bromide and an
excess of mercuric bromide. Treatment of decylmercuric
bromide with alcoholic potassium hydroxide and dry acetylene
gave bisdecylmercuric acetylide, $C_{10}H_{21}HgC \equiv CHgC_{10}H_{21}$.
Several lower homologs of both series were also made.

Kharasch and Marker (47) reported that the n-hexadecyl
radical was one of the least electronegative of all those
examined. The unsymmetrical molecules containing the hexa-
decyl group were not described, however, and they have not
yet been reported.

Slotta and Jacobi (27) were interested in the bacteri-
cidal properties of alkylmercuric salts. They prepared a
great many of them, among which were several n-hexadecyl-
mercuric salts. Hexadecylmercuric bromide was prepared from
the Grignard reagent and mercuric bromide, in 90% yield.
The bromide was treated with alcoholic potassium hydroxide
and then an excess of dilute hydrochloric or hydriodic acid,
to prepare, respectively, hexadecylmercuric chloride and
hexadecylmercuric iodide. The intermediate hexadecylmercuric
hydroxide was also isolated. The properties of these four
compounds are shown in Table 1.

---

47. Kharasch and Marker, ibid., 48, 3130 (1926).

Table 1

Hexadecylmercuric Salts

Anion	Melting point ($^\circ$C)	Solubility in g./100 g. of alcohol at 78°	Solubility in g./100 g. of chloroform at 18°
bromide	101.5	1.9	0.9
chloride	102	2.5	0.74
iodide	82	1.4	2.5
hydroxide	78	---	---

In addition to these compounds, the cyanide, acetate, nitrate, sulfate, bromide, chloride, and iodide of each of the alkyl-mercury derivatives from methyl to n-heptyl were described.

Mercuric acetate dissolved in methanol or water reacted with olefins such as nonylene, decylene, dodecylene, hexa-decylene, and heneicosylene. The object of this study was to determine the "mercuration number" of hydrocarbons, and the products were not isolated (48). Matejka (49) found that mercuric acetate reacted with cinnamic acid and cetyl alcohol to give

$$C_6H_5CH-----CH---C = O$$
$$OC_{16}H_{33} \qquad Hg---O$$
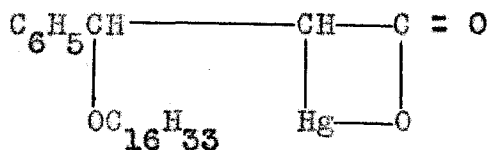
which was soluble in hot sodium hydroxide solution and in

48. Tausz, Petroleum, 13, 649 (1918) /Chem. Zentr., II, 125 (1919)/.

49. Matejka, Ber., 69, 274 (1936).

ether. This and other mercury derivatives of cinnamic acid, safrol, and coumarin, were considered to be of possible bactericidal value.

Pontz (7) attempted unsuccessfully to prepare n-octadecylmercuric bromide from octadecylmagnesium bromide and mercuric chloride, although Marvel and Gould (50) had found that RMgBr and $HgCl_2$ always gave mixtures of RHgBr and RHgCl. Pontz also prepared n-octadecylmercuric bromide from the Grignard reagent and mercuric bromide, but did not analyze his product. He succeeded in making octadecylmercuric cyanide, and tried unsuccessfully to obtain octadecylmercuric nitrate.

Compounds in which the long alkyl chain is not directly attached to the mercury atom have been prepared. Phenylmercuric dodecyl sulfate and phenylmercuric dodecanesulfonate were found to be strongly germicidal, and of relatively low toxicity (51). Phenylmercuric decyl sulfate was described as suitable for use in cleaning and sterilizing bottles (52). Phenylmercuric hydroxide reacted with cetyl alcohol and other long-chained alcohols to form the alcoholates, such as $C_{16}H_{33}OHgC_6H_5$. Compounds of this type had strong antiseptic or germicidal action (53). Phenylmercuric and p-tolyl mercuric salts of the fat acids were suggested as derivatives

50. Marvel and Gould, J. Am. Chem. Soc., 44, 153 (1922).

51. Andersen, U. S. Patent, 2215457 /Chem. Abstr., 35, 858 (1941)7.

52. Johnson and Allison, U. S. Patent, 2216842 /Chem. Abstr., 35, 1940 (1941)7.

53. Andersen, U. S. Patent, 2056945 /Chem. Zentr., I, 1193 (1937)7.

of the acids (54).

Novelli (55) mercurated several dialkylfluoresceins, and
found that the antiseptic activity increased with the increas-
ing length of the side-chain, R, in the series, n-propyl,
n-butyl, and n-heptyl.
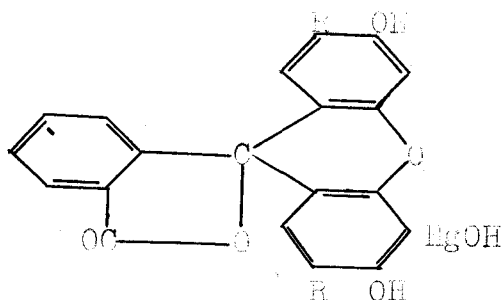
C. Compounds of the third periodic group.

Triisoamylboron has been prepared by Krause and Nitsche
(56) from the Grignard reagent and boron fluoride, in nearly
quantitative yield. It was a liquid with a rather unpleasant
odor remindful of that of amyl alcohol. It did not explode
readily in air, but decomposed with the evolution of white
fumes. Water alone did not react with it, but water in con-
junction with air gradually formed isoamylboric acid, which
was a solid melting at 169°. Snyder, Kuck, and Johnson (57)
obtained tetradecaneboronic acid, $C_{14}H_{29}B(OH)_2$, from

54. Ford, Iowa State Coll. J. Sci., 12, 121 (1937).

55. Novelli, Anales farm. bioquim., 4, 29 (1933)/Chem. Abstr.,
    30, 6129 (1936)/.

56. Krause and Nitsche, Ber., 54, 2784 (1921).

57. Snyder, Kuck, and Johnson, J. Am. Chem. Soc., 60, 105
    (1938).

n-tetradecylmagnesium bromide and n-butyl borate. After the octacosane (formed during the preparation of the Grignard reagent) had been allowed to crystallize from alcohol solution, the alkylboronic acid was obtained by evaporation of the alcohol filtrates. It formed waxy crystals which melted over a wide range. No analysis was reported.

Leone (58) prepared what was probably a mixture of dioctylaluminum bromide and octylaluminum dibromide by the reaction of n-octyl bromide and aluminum in absence of ether. The reaction of alkyl iodides with aluminum was found to proceed very readily in the presence of a small amount of ether. Triisoamylaluminum is the highest known homolog of the R_3Al type (59). It was prepared from diisoamylmercury and aluminum metal.

Dihexylthallium fluoride, chloride, bromide, iodide, and nitrate were prepared by Krause and Dittmar (60). Molecular weight determinations on di-n-hexylthallium fluoride showed it to be highly associated in benzene solution; the molecular weights varied from about two to seven times the simple molecular weight. The highest known R_3Tl compound is triiso-butylthallium (61), which was prepared from isobutylthallium bromide and the Grignard reagent.

58. Leone, Gazz. chim. ital., 55, 294 (1925).

59. Louise and Roux, Bull. soc. chim., 50, 497 (1888).

60. Krause and Dittmar, Ber., 63, 1953 (1930).

61. Birch, J. Chem. Soc., 1132 (1934).

D. Compounds of the fourth periodic group.

Taurke (62) obtained tetraisoamylsilicon from silicon tetrachloride by a Wurtz reaction, with isoamyl chloride and sodium metal. Tetra-n-amylsilicon has been prepared by the same method (63). The ortho-ester, hexyltriethoxysilicon, has been prepared also (64). Apparently no longer chains have been attached directly to silicon. Backer and Stienstra (65) made the tetracetyl ester of tetrathiosilicic acid, from silicon tetrachloride and the sodium salt of cetylmercaptan. The silicon, germanium, and tin compounds of this type were found to be isomorphous. These are, of course, not organo-metallic compounds.

Tetraisoamylgermanium was prepared from isoamylmagnesium bromide and germanium tetrachloride in 87% yield (66).

Krause and co-workers (67,68,69) prepared tetraisoamyltin

62. Taurke, Ber., 38, 1663 (1905).

63. Schumb, Ackerman, and Saffer, J. Am. Chem. Soc., 60, 2486 (1938).

64. Adrianov and Gribanova, J. Gen. Chem. (U.S.S.R.), 8, 558 (1938) /Chem. Abstr., 32, 7892 (1938)/.

65. Backer and Stienstra, Rec. trav. chim., 54, 607 (1935).

66. Tabern, Orndorff, and Dennis, J. Am. Chem. Soc., 47, 2039 (1925).

67. Krause, Ber., 51, 1447 (1918).

68. Krause and Weinberg, ibid., 63, 381 (1930).

69. Grüttner and Krause, ibid., 50, 1802 (1917).

and several isoamyltin halides. Jones, Evans, Gulwell, and Griffiths (70) made tetra-n-octyltin and some of its lower homologs from the Grignard reagents and stannic chloride. They measured the refractive indices, densities, and heats of combustion of a number of tin, lead, and mercury alkyls, and calculated the molecular refractions, molecular volumes, and heats of formation. The atomic refractivity of tin was found to be 13.87 (sodium D). The boiling point of tetra-n-octyltin was 268° at 10 mm.

Zartman and Adkins (71) hydrogenated tetra-n-heptyllead over a nickel catalyst for six hours at 200°. They obtained a 62% yield of n-tetradecane, together with some heptene and probably some heptane. The tetraheptyllead was supplied by Dr. G. Calingaert, and its preparation and properties were not described. The highest R_4Pb homologs whose properties are recorded in the literature are tetra-n-amyllead (70) and tetraisoamyllead (72). The latter was prepared in three steps from the Grignard reagent and lead chloride: the crude first product was converted to triisoamyllead bromide by treatment with bromine at -75°; then more RMgCl was added. There resulted a 75-80% yield of tetraisoamyllead, which was purified by steam distillation. It solidified in a bath

70. Jones, Evans, Gulwell, and Griffiths, J. Chem. Soc., 39 (1935).

71. Zartman and Adkins, J. Am. Chem. Soc., 54, 3398 (1932).

72. Grüttner and Krause, Ber., 50, 278 (1917).

at -75°. Triisoamyllead chloride (73), bromide (72), and
iodide (73), and diisoamyllead dichloride and dibromide (72)
have been prepared. Jones and co-workers (70) made di-n-
amyllead dichloride, dibromide, and sulfate.

Pontz (7) reacted triethyllead chloride (74) with
n-octadecylmagnesium bromide and obtained triethyloctadecyl-
lead. Diethyllead dichloride (74) and the n-octadecyl Grignard
reagent gave diethyldioctadecyllead (7). Triphenyltin chloride
and octadecylmagnesium bromide yielded octadecyltriphenyltin.

Ford (54) used the triphenyllead salts of the fat acids
as derivatives of the latter.

E. Compounds of the fifth periodic group.

Jackson, Davies, and Jones (75) made tri-n-octylphosphorus
from the Grignard reagent and phosphorus trichloride. It was
stable at 250°; it oxidized readily at room temperature, but
did not form addition compounds with methyl iodide, mercuric
iodide, or carbon disulfide. Triheptyl- and trihexylphos-
phorus were also described.

Several phosphonium salts containing long alkyl chains
have been prepared. Dodecyltrimethylphosphonium bromide,
ethylhexadecyldimethylphosphonium chloride, and

73. Klippel, Jahresber., 383 (1860).

74. Gilman and Robinson, J. Am. Chem. Soc., 52, 1975 (1930).

75. Jackson, Davies, and Jones, J. Chem. Soc., 2109 (1931).

diethyldioleylphosphonium sulfate were described as stripping agents for the removal of dyes from textiles, leather, or paper. They were all water soluble (76). On the other hand, triethylhexadecylphosphonium bromide and triethyldodecylphosphonium bromide were used to improve the fastness of dyes to water and perspiration (77). Triethylhexadecylphosphonium bromide and triethyloctadecylphosphonium bromide were used for breaking oil-water emulsions (78). The trilaurylamide of phosphorous acid and similar compounds were used as lubricants (79).

Trioctylarsenic was prepared from n-octylmagnesium bromide and arsenic trioxide in 70% yield. The odor was said to resemble that of octyl alcohol (80). Jones, Dyke, Davies, Griffiths, and Webb (81) presented a collection of data on the physical properties of tertiary arsines. The boiling point at 10 mm. was found to be given by the expression

$$t_{10mm.} = 18.30 \ M^{0.555} - 273.1$$

76. I. G. Farbenindustrie Akt.-Ges., British Patent 434,810 /Chem. Zentr., I, 1118 (1936)7.

77. Evans, Piggott, and Woolvin, British Patent 437,273 /Chem. Zentr. I, 1713 (1936)7.

78. de Groote, U. S. Patent 2106239 /Chem. Zentr., I, 3867 (1938)7.

79. Flint and Salzberg, U. S. Patent 2151380 /Chem. Zentr., II, 301 (1939)7.

80. Gryszkiewicz-Trochimowski, Roczniki Chem., 8, 250 (1928) /Chem. Abstr., 22, 4523 (1928)7.

81. Jones, Dyke, Davies, Griffiths, and Webb, J. Chem. Soc., 2284 (1932).

where M denotes the molecular weight of the tri-n-alkyl-arsenic. The atomic refraction due to arsenic was 11.96 (sodium D line).

Triethyloctadecylarsonium bromide was used in conjunction with amylase in the enzymatic desizing of heavily sized textile goods (82).

Dyke, Davies, and Jones (83) reported that tri-n-hexyl-antimony, prepared by the reaction of antimony trichloride with the Grignard reagent, boiled at 190° at 10 mm. with partial decomposition and the liberation of antimony. Tseng and Shih (84), however, obtained tri-n-heptylantimony by the same method, in 18% yield. They reported a boiling point of 229-231° at 50 mm. Triheptylantimony reacted with iodine to give the diiodide; with mercuric oxide it yielded triheptylantimony oxide. The product obtained on evaporation of the ether solution was $R_3Sb_3O_4$.

Davies, Norvick, and Jones (85) prepared tri-n-amyl-bismuth from the Grignard reagent and bismuth trichloride. The higher alkylbismuthines, such as this one, were said to have no disagreeable odor. It was observed that the trialkyl

82. Kalle and Co. Aktiengesellschaft, British Patent 455,804
    /Chem. Zentr., I, 2300 (1937)/.

83. Dyke, Davies, and Jones, J. Chem. Soc., 463 (1930).

84. Tseng and Shih, J. Chinese Chem. Soc., 4, 183 (1936)
    /Chem. Abstr., 31, 669 (1937)/.

85. Davies, Norvick, and Jones, Bull. soc. chim., 49, 187
    (1931).

derivatives of nitrogen, phosphorus, arsenic, antimony, and bismuth became less stable thermally with increasing atomic weight of the central element. The oxidizability increased with increasing atomic weight.

F. Compounds of the sixth, seventh, and eighth periodic groups.

Of the twenty-six elements of these groups only two or three give promise of forming compounds of any stability with long alkyl chains. Aromatic, but not aliphatic, organomanganese compounds can be prepared readily from manganese halides and the Grignard reagents. They are reactive and inflammable (86). Druce (87) obtained trimethylrhenium from rhenium trichloride and methylmagnesium iodide. Pope and Peachey (88) prepared trimethyl platinum iodide from platinic chloride and methylmagnesium iodide. It was very stable and unreactive. With silver hydroxide in acetone it gave trimethylplatinic hydroxide, from which several other trimethylplatinum salts were prepared. It seems very probable that longer alkyl groups could be substituted for the methyl groups in these compounds.

Chromium, while it forms numerous aryl compounds (89),

86. E. Bindschadler, unpublished work.

87. Druce, J. Chem. Soc., 1129 (1934).

88. Pope and Peachey, J. Chem. Soc., 95, 571 (1909).

89. Hein and co-workers, Ber., 54, 1905, 2708, 2727 (1929); ibid., 59, 362, 751 (1926); ibid., 61, 2255 (1928); ibid., 62, 1151 (1929); J. prakt. Chem., 132, 59 (1931); Ber., 71, 1966 (1938); J. prakt. Chem., 153, 160 (1939).

apparently does not give stable alkyl derivatives (90). Molyb-
denum (91) and tungsten (92) and the majority of the elements
of the eighth group have given little indication of the forma-
tion of organometallic compounds (93).

G. Physiological activity of long-chained compounds.

The theory of lipophilic chemotherapeuticals has been
outlined briefly by Bergmann and Haskelberg (94). They explain
in their introductory paragraphs,

"The systematic synthesis of substances expected
to have chemotherapeutical value is based on
Ehrlich's postulate that they should have affinity
for the tissue forming the cell-wall of the para-
site but not for that of the host. There are
still a few maladies in which chemotherapeutical
investigations have had but little success, e.g.,
tuberculosis, leprosy, and parasitic diseases of
the Theileria type.

"In seeking a new type of chemotherapeutical,
intended to have affinity to the lipoids and not
to the proteins, we were influenced by two con-
siderations: (i) the cell-walls of the tubercle
and of leprosy bacilli are known to consist largely
of lipoid material, so it was expected that they
would exhibit a selective affinity for lipophilic
substances; (ii) such substances should be effec-
tive in all cases in which the infected tissue is
lipoidal in character."

90. Kondyrew and Fomin, J. Russ. Phys.-Chem. Soc., 47, 190
    (1915) /Chem. Zentr., I, 833 (1916)/.

91. Gasopoulos, Praktika, 7, 180 (1932) /Chem. Zentr., II, 534
    1933)/.

92. Weichsfelder and Theide, Ann., 447, 64 (1926).

93. Gilman and Lichtenwalter, J. Am. Chem. Soc., 61, 957 (1939).

94. Bergmann and Haskelberg, J. Chem. Soc., 1, (1939).

Hoyt (95) has reviewed the physiological effects of long-chained compounds in general. He concluded that

"....desirable physiological properties may
appear again in some of the series as the ali-
phatic chain is lengthened. However, there
remains still the difficulty of the low solubil-
ity in water, a characteristic of most of the
long-chained members of these series.... A...
way out of the difficulty would be a means of
testing which would give comparable results for
both soluble and insoluble homologs...."

Several instances have been mentioned previously of recent work on long-chained therapeuticals, especially mercurials (26,49,51,52,53,55,94). Some of these were said to be germicidal or bactericidal, but no pharmacological reports were given.

Clark (96) has outlined the difficulty of correlating the chemical structure and therapeutic value of chemotherapeutic agents. In a homologous series of drugs some members may not only fail to produce the action typical of the series, but may even antagonize the action of the other members. So it is not necessary to follow the line of homology in preparing lipophilic therapeuticals, although this still seems an advisable course.

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95. F. W. Hoyt, Ph. D. Thesis, Iowa State College (1940).

96. Clark, in Heffter, Heubner, and Schüller's "Handbuch der experimentellen Pharmakologie," 4, 206, Springer, Berlin (1937).

III. EXPERIMENTAL

A. Organomercury compounds--Dialkylmercury types.

1. Didodecylmercury.-- Six and one-tenth grams of do-
decyl bromide (0.0246 mole) dissolved in 5 cc. of dry ether
were slowly added with stirring to 0.6 g. (0.0246 atom) of
magnesium turnings suspended in 20 cc. of ether. The excess
magnesium was filtered out, and 6.8 g. of dodecylmercuric
bromide (0.0151 mole) was added. The mixture was refluxed for
fifty minutes. A color test number I (38) at the end of one
and one-half hours was negative. The mixture was hydrolyzed
and the ether allowed to evaporate. The residue was filtered,
washed with water, and dried. It was first recrystallized
from about 200 cc. of 95% alcohol, to give 3.7 g. of material
which melted at about 40-80°. This was separated by recrystal-
lization from petroleum ether into 0.2 g. of dodecylmercuric
bromide, m.p. 108-109°, and a petroleum ether solution of
didodecylmercury. More of the latter was recovered by ex-
tracting the material not dissolved in the 200 cc. of hot
alcohol, with petroleum ether. The petroleum ether solutions
were evaporated, giving a solid melting at 40-60°. One re-
crystallization from ethyl acetate and methanol narrowed the
range to 41-42°. Three recrystallizations from ethyl acetate
and alcohol yielded pure didodecylmercury melting at 44-44.5°.

The compound was decomposed with fuming sulfuric acid and 30% hydrogen peroxide, and the mercury was precipitated and weighed as the sulfide (97).

Anal. Calc'd. for $C_{24}H_{50}Hg$: Hg, 37.20%. Found: Hg, 37.44%.

A second, larger run was made using 26.4 g. of dodecyl bromide (0.106 mole), 2.58 g. of magnesium, and 100 cc. of ether to make the Grignard reagent. To the filtered reagent were added 12.9 g. of dodecylmercuric bromide (0.0287 mole) and 8.95 g. of mercuric chloride (0.0318 mole). The mixture was refluxed, hydrolyzed; the ether was distilled, and the residue filtered off. This was dissolved in petroleum ether (B) (98) and the excess dodecylmercuric bromide (99) was filtered off. The latter weighed 9.0 g., (0.02 mole) or 33% based on the total mercury added.

The petroleum ether filtrate was evaporated to dryness and the residue was recrystallized from ethyl acetate and methanol. The yield was 17.5 g. (0.0325 mole), or 51.2% of the theoretical. The melting point was 40-41°. This crude material was not purified further.

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97. Tabern and Shellberg, Ind. Eng. Chem., Anal. Ed., 4, 401 (1932).

98. The letters A, B, and D are used to denote petroleum ether fractions 30-35°, 60-68°, and 85-105°, respectively.

99. Actually a mixture of bromide and chloride, according to Marvel and Gould (Ref. 50), but by analysis almost pure bromide (44.6% Hg).

2. _Ditetradecylmercury._-- Ten and four-tenths grams of n-tetradecyl bromide (0.0389 mole) was dissolved in 10 cc. of ether and added slowly to 0.95 g. of magnesium, a small crystal of iodine, and 30 cc. of ether. To the filtered Grignard reagent was added directly 6.3 g. (0.0175 mole) of mercuric bromide. This caused rapid refluxing for a short time. The mixture was stirred for two hours, then hydrolyzed, and the ether was evaporated. The residue was filtered, washed with water, and dried. It was recrystallized from petroleum ether to remove the tetradecylmercuric bromide. The yield of the latter was 4.1 g. (0.00858 mole), melting at 108-110°, which accounted for 49% of the mercury added.

Evaporation of the petroleum ether (B) filtrate gave 3.4 g. (0.0057 mole), or 32.6% of the theoretical yield of di-tetradecylmercury, melting at 47-49.5°. It was recrystallized four times from ethyl acetate to give pure ditetradecylmercury melting at 53-54°.

Anal. Calc'd. for $C_{28}H_{58}Hg$: Hg, 33.70%. Found: Hg, 33.0%.

3. _Dihexadecylmercury._-- Twenty-five cubic centimeters of 0.378 N n-hexadecylmagnesium bromide was added to 4.75 g. (0.0094 mole) of n-hexadecylmercuric bromide in 35 cc. of dry ether. The mixture was stirred and refluxed until the solid had nearly dissolved. It was then cooled, filtered and washed. It was recrystallized from low-boiling petroleum ether to give

3.4 g. (55%) of crude dihexadecylmercury melting at 59-61°.
It was recrystallized twice from petroleum ether (A). The
pure dihexadecylmercury melted at 61-62°.

Anal. Calc'd. for $C_{32}H_{66}Hg$: Hg, 30.79%. Found: Hg,
30.96%.

4. Dioctadecylmercury.-- Seven and four-tenths grams
(0.022 mole) of n-octadecyl bromide in 16 cc. of ether was
added slowly to 0.54 g. of magnesium in 20 cc. of ether. The
Grignard reagent was filtered through glass wool and diluted
with 50 cc. of dry ether. To this was added 10.5 g. (0.0196
mole) of octadecylmercuric bromide. No reaction was noted.
The mixture was hydrolyzed and the ether was evaporated. The
residue was filtered, washed with water, and dried. It was
crystallized from petroleum ether (B - D) to give a material
melting at 65-105° (a mixture of R_2Hg and RHgBr) which weighed
8.1 g. This was recrystallized from 100 cc. of petroleum
ether (D) to give 5.6 g. of pure octadecylmercuric bromide,
m.p. 111-112.5° (53.3% of the original). The petroleum ether
filtrates were distilled to remove the solvent. The residue
weighed 9.9 g., and melted at 63-65°. It was recrystallized
from ethyl acetate twice to give 3.7 g. melting at 66-66.5°,
then once from petroleum ether (B). The melting point was
then 66.5-67° (7).

The compound was analyzed by the method of Tabern and
Shellberg (97).

Anal. Calc'd for $C_{36}H_{74}Hg$: Hg, 28.35%. Found: Hg,
28.35%.

B. Organomercury compounds--Alkylmercuric salts.

1. Dodecylmercuric bromide.-- Twelve and one-half grams
of n-dodecyl bromide (0.05 mole) in 20 cc. of ether was added
slowly to 1.22 g. of magnesium in 80 cc. of ether. The
Grignard reagent was transferred as usual. It was treated with
16.2 g. of mercuric bromide by the Soxhlet extraction method.
Extraction was continued for twenty-four hours. The product
was then hydrolyzed with water and ammonium bromide, filtered
and washed with water, alcohol, and ether. The crude material
melted at 100-110° and weighed 10.87 g. (53.8%). It was re-
crystallized twice from alcohol to give dodecylmercuric
bromide (25), melting at 108-108.7°. It was analyzed for
mercury by the method of Tabern and Shellberg (97).

Anal. Calc'd for $C_{12}H_{25}HgBr$: Hg, 44.60%. Found: Hg,
45.37%.

2. Dodecylmercuric acetate.-- From 17 g. of silver nitrate
and 13.6 g. of sodium acetate was obtained 11.6 g. (69.5% of
theoretical) of silver acetate. One and thirteen-hundredths
grams of silver acetate (0.00667 mole) were stirred and re-
fluxed for one-half hour with 100 cc. of 95% alcohol and 3 g.
of dodecylmercuric bromide. The silver bromide was filtered
off. When the filtrate was cooled in ice a white precipitate
of dodecylmercuric acetate formed. The crude material weighed
1.72 g. (0.004 mole, or 60% of theoretical) and melted at 64-
65°. Recrystallization from petroleum ether did not change

the melting point. The product was analyzed as usual by the method of Tabern and Shellberg (97).

Anal. Calc'd for $C_{14}H_{28}O_2Hg$: Hg, 46.75%. Found: Hg, 46.5%.

3. **Attempts to prepare dodecylmercuric arsenate.** -- Three and one-quarter grams of didodecylmercury (0.006 mole) and 1.76 g. (0.002 mole) of mercuric arsenate (100) were stirred and refluxed for five hours. The only product soluble in hot alcohol was didodecylmercury. There was very little evidence that the arsenate had formed.

Ten and two-tenths grams of silver nitrate dissolved in water was added to a solution of 6.25 g. of disodium arsenate. The brown silver arsenate (101) was then filtered off and washed. The yield was 7.5 g. (81% of theoretical).

Five grams of dodecylmercuric iodide (0.01 mole) and 1.55 g. of silver arsenate were stirred and refluxed with 100 cc. of 95% alcohol for one-half hour. The mixture was filtered hot to remove silver iodide. Not all of the silver arsenate had reacted. The alcohol solution deposited a powdery white solid, m.p. 87-89°. It was crystallized from petroleum ether (B), then from methanol. The product was then no longer very soluble in petroleum ether (B); it was extracted with

100. Haack, Ann., 262, 181 (1891).

101. Friend, "A Textbook of Inorganic Chemistry," vol. 2, Griffin, London (1924), p. 318.

250 cc. of this solvent, hot. The undissolved residue melted at 105°. This was analyzed for mercury (102).

Anal. Calc'd for $C_{36}H_{75}O_4Hg_3As$: Hg, 48.2%. Found: Hg, 47.1%.

No further attempt was made to purify or analyze this material. The theoretical mercury content of the starting material, dodecylmercuric iodide, is only 40.37%.

It is to be noted that the directions for preparing mercuric arsenate given in Friend (103) are in error. Haack (100) used mercuric nitrate, not mercurous nitrate as in Friend.

4. Dodecylmercuric chloride.-- Three and one-quarter grams of didodecylmercury (0.006 mole) and 1.64 g. of mercuric chloride were refluxed with 100 cc. of 95% alcohol. The solution was cooled and filtered. The product was recrystallized from petroleum ether (B). The yield was 3.3 g. (67.8%) of dodecylmercuric chloride melting at 114°. It was recrystallized from 95% alcohol, and melted at 114-114.5°. The compound was analyzed as usual (97).

Anal. Calc'd for $C_{12}H_{25}HgCl$: Hg, 49.5%. Found: Hg, 49.2%.

102. Rüdisüle, "Nachweis, Bestimmung und Trennung der chemischen Elemente," 1. Nachtragsband, part 1, p. 659, P. Haupt, Bern (1936).

103. Friend, l.c., vol. 3, part 2, p. 294 (1926).

5. <u>Dodecylmercuric iodide</u>.-- Two and sixteen-hundredths grams of didodecylmercury (0.004 mole) and 1.78 g. of mercuric iodide were refluxed with 50 cc. of dry ether for fifteen minutes. The red mercuric iodide disappeared. The solution was cooled and filtered; the solid was washed with petroleum ether. The product was recrystallized from petroleum ether (B) to give 1.9 g. (47%) of dodecylmercuric iodide, melting at 91°. The product was analyzed by a modification of the method given by Tabern and Shellberg, for mercury in the presence of iodine (97).

<u>Anal</u>. Calc'd for $C_{12}H_{25}HgI$: Hg, 40.37%. Found: Hg, 40.18%.

6. <u>An attempt to prepare dodecylmercuric nitrate</u>.-- Five grams of dodecylmercuric bromide (0.011 mole) and 2.1 g. of silver nitrate were refluxed with 160 cc. of 95% alcohol. The silver bromide was filtered off (weight 1.90 g., or 0.01 mole). The alcohol filtrate was cooled to give 4.1 g. (77%) of dodecyl-mercuric nitrate, melting at 77-79°.

<u>Anal</u>. Calc'd for $C_{12}H_{25}O_3NHg$: Hg, 46.44%. Found: Hg, 48.4%.

The product was recrystallized from methanol; m.p. 77-80°.

<u>Anal</u>. Found: Hg, 48.3%

Recrystallization from petroleum ether (B) gave a product melting at 76.5-78.5°.

<u>Anal</u>. Found: Hg, 48.5%.

An aqueous suspension gave no darkening with hydrogen
sulfide. No further attempts were made to purify or analyze
this compound.

7. Dodecylmercuric phosphate.-- An aqueous solution of
28.6 g. of disodium phosphate dodecahydrate and a solution of
41.2 g. of mercuric nitrate in dilute nitric acid were mixed.
The precipitated mercuric phosphate was filtered and washed.
The yield was 32.8 g., which was almost quantitative.

Three and one-quarter grams of didodecylmercury (0.006
mole) and 1.58 g. of mercuric phosphate were refluxed with 50
cc. of absolute alcohol overnight. The mixture was filtered
hot and the residue extracted with hot 95% alcohol. The fil-
trate deposited a voluminous white precipitate on cooling.
The yield was 3.45 g. (71.5%) of dodecylmercuric phosphate,
melting at 83°, not sharply. It was recrystallized from
petroleum ether (B), then from alcohol. The melting point was
84-86°. It was analyzed by the method of Tabern and Shellberg
(97).

Anal. Calc'd for $C_{36}H_{75}O_4PHg_3$: Hg, 49.97%. Found: Hg,
49.49%.

8. Dodecylmercuric sulfate.-- Three and one-quarter grams
(0.006 mole) of didodecylmercury and 1.77 g. of mercuric sul-
fate were refluxed with 50 cc. of dry ether and 10 cc. of
absolute alcohol. To this were added later 10 cc. of water and
20 cc. of petroleum ether. (The addition of water was not

wise since water decomposes mercuric sulfate.) The mixture
was poured into 200 cc. of water and the organic solvents
were allowed to evaporate. The residue was filtered and
washed. It was extracted with hot petroleum ether to remove
any unreacted bismercurial. The residue was recrystallized
from 95% alcohol; this yielded 0.75 g. (15%) of dodecylmer-
curic sulfate, melting at 160-161°. From the filtrates there
was recovered 2.3 g. (71%) of didodecylmercury, m.p. 40-41°.

Anal. Calc'd for $C_{24}H_{50}O_4SHg_2$: Hg, 47.99%. Found:
Hg, 48.10%.

9. Tetradecylmercuric bromide.-- Thirteen and nine-
tenths grams of tetradecyl bromide (0.05 mole) in 40 cc. of
ether was added slowly to 1.22 g. of magnesium in 50 cc. of
ether. The Grignard reagent was transferred as usual; the
total volume was about 88 cc. Titration showed this to be
0.392 normal, so the yield was 0.0354 mole, or 70.8% of the
theoretical. The tetradecyl bromide used was Eastman stock
which had been on hand for some time and had turned yellow-
brown; partial decomposition may account for the unusually low
yield.

Eleven and three-tenths grams of mercuric bromide (0.0314
mole) was placed in a Soxhlet thimble and extracted as usual
into the remaining Grignard solution, under nitrogen. It was
extracted for 23 hours, after which very little (0.5 g.) was
left in the thimble. A color test number I (38) on the

solution was negative. The mixture was hydrolyzed, filtered, and washed. It was recrystallized from 250 cc. of methanol. The filtrate was used to extract the undissolved portion, etc., four times. The product melted at 110-111°. The yield was 7.0 g. (48.8%). A small portion was recrystallized twice from methanol. It melted at 110-110.5°. It was analyzed for mercury by the method of Tabern and Shellberg (97).

Anal. Calc'd for $C_{14}H_{29}HgBr$: Hg, 41.98%. Found: Hg, 42.53%, 42.69%.

Bromine analysis was attempted by the Parr bomb method. The results were low.

Anal. Calc'd for $C_{14}H_{29}HgBr$: Br, 16.73%. Found: Br, 14.3%, 14.3%.

10. Hexadecylmercuric bromide.-- This compound, and the chloride and iodide, have been reported by Slotta and Jacobi (26), but the melting points observed were not consistent with those found in this research for the other long-chained mercuric halides; therefore the preparations were repeated.

Ninety-nine cubic centimeters of 0.482 N n-hexadecyl-magnesium bromide in ether was treated with 16.7 g. of mercuric bromide (0.0477 mole). The mixture was refluxed and stirred for ten and one-half hours, then hydrolyzed. The ether was removed by evaporation, and the residual solid was filtered and dried. It was recrystallized from petroleum ether (B) to give 15.3 g. (63.3%) of hexadecylmercuric bromide, melting at

110-111°. Recrystallization from ethyl acetate raised the melting point to 110.5-111.5°.

Anal. Calc'd for $C_{16}H_{33}BrHg$: Hg, 39.65%. Found: Hg, 40.42%, 40.15%.

11. Hexadecylmercuric chloride.-- One and three-tenths grams (0.002 mole) of dihexadecylmercury and 0.55 g. of mercuric chloride were refluxed with 60 cc. of ether. The mixture was cooled, filtered, and washed with alcohol. It was recrystallized from petroleum ether (D), then from ethyl acetate. The yield was 0.8 g. (43%) of hexadecylmercuric chloride, melting at 114-115°.

Anal. Calc'd for $C_{16}H_{33}ClHg$: Hg, 43.46%. Found: Hg, 43.25%.

12. Hexadecylmercuric iodide.-- One and three-tenths grams of dihexadecylmercury (0.002 mole) and 0.91 g. of mercuric iodide were refluxed with 40 cc. of ether for fifteen minutes. The solution was cooled and the product was filtered off. It was recrystallized from petroleum ether (B). The yield was 1.3 g. (58.7%) of hexadecylmercuric iodide, melting at 93-93.5°.

Anal. Calc'd for $C_{16}H_{33}IHg$: Hg, 36.28%. Found: Hg, 35.98%.

13. Octadecylmercuric bromide.-- Eighteen and one-half grams of n-octadecyl bromide (0.0555 mole) in 20 cc. of ether

was added slowly to 1.35 g. of magnesium in 40 cc. of ether.
The Grignard reagent was transferred as usual. To this was
added quickly 18.0 g. (0.05 mole) of mercuric bromide. The
mixture refluxed rapidly. It was warmed and stirred, and
ether was added to dilute the mixture. It was hydrolyzed and
the ether was evaporated; the residue was filtered and washed.
The crude material weighed 22.6 g. (84.5% of theoretical).
It was recrystallized twice from petroleum ether (B,D), and
melted at 110-111° (104). It was analyzed by the method of
Tabern and Shellberg (97).

Anal. Calc'd for $C_{18}H_{37}HgBr$: Hg, 37.57%. Found: Hg,
37.28%.

14. **Octadecylmercuric chloride.**-- Seventy-one hundredths
of a gram of dioctadecylmercury (0.001 mole) and 0.27 g. of
mercuric chloride were refluxed with ether for one and three-
quarter hours. The mixture was cooled and filtered. The
product was recrystallized from petroleum ether (D). The
melting point was 115-116°; the yield was 0.85 g. (87% of the
theoretical). The compound was analyzed as usual (105).

Anal. Calc'd for $C_{18}H_{37}HgCl$: Hg, 40.97%. Found: Hg,
41.20%.

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104. D. F. Pontz (unpublished work) reported 111-112°, but did
not analyze his product.

105. D. F. Pontz tried to make this compound from octadecyl-
magnesium bromide and mercuric chloride. His product
melted at 113-113.5° and was probably a mixture of RHgBr
and RHgCl (unpublished work).

Table 2

Melting Points of Organomercury Compounds

R	$n\text{-}C_{12}H_{25}$	$n\text{-}C_{14}H_{29}$	$n\text{-}C_{16}H_{33}$	$n\text{-}C_{18}H_{37}$
R_2Hg	44-44.5°	53-54°	61-62°	66.5-67°
RHgCl	114-114.5	---	114-115	115-116
RHgBr	108-108.7	110-110.5	110.5-111.5	110-111
RHgI	91	---	93-93.5	---
$RHgC_2H_3O_2$	64-65	---	---	---
$(RHg)_2SO_4$	160-161	---	---	---
$(RHg)_3PO_4$	84-86	---	---	---

C. Organolead compounds--Trialkyllead salts.

1. Tridodecyllead chloride.-- Seventeen and one-half grams of dodecyl bromide (0.0702 mole) in 20 cc. of dry ether was added slowly to 1.75 g. of magnesium turnings in 80 cc. of ether. The Grignard reagent was titrated with acid; the normality was 0.551; the volume was about 118 cc.; so the yield was 92.8% of theoretical.

To the remaining 113 cc. of Grignard solution was added 7.3 g. of lead chloride. The solution and suspended lead salt immediately darkened, and the ether refluxed rapidly. The color of the mixture changed from reddish, to greenish, and then to gray. It was refluxed and stirred for fifteen hours; it was then poured into ice containing 15 g. of ammonium

chloride. The ether was evaporated, and the residue was
filtered off and dried. It was extracted with 75 cc. of hot
chloroform. Some yellowish, slightly soluble material re-
mained after the extraction, besides the expected lead metal,
and more of this yellowish material separated as the chloro-
form filtrate cooled. This filtrate was evaporated to about
20 cc. and refiltered. The solid obtained was recrystallized
from ethyl acetate by the addition of alcohol. The recrystal-
lization from ethyl acetate was repeated three times to give
a white powder melting at 63.5°. It was analyzed for lead by
decomposition with sulfuric and nitric acids, and precipita-
tion as lead sulfate in 50% alcohol (106).

Anal. Calc'd for $C_{36}H_{75}PbCl$: Pb, 27.60%. Found: Pb,
27.46%.

Tridodecyllead chloride was also prepared from dodecyl-
magnesium chloride and lead chloride, since there was some
doubt that the halogen in the first preparation was entirely
chlorine:

To the Grignard reagent prepared from 23.5 g. (0.115
mole) of dodecyl chloride and 2.5 g. of magnesium in 125 cc.
of ether was added 18.9 g. (0.068 mole) of lead chloride.
This was hydrolyzed with water and ammonium chloride, the
ether was evaporated, and the precipitate was filtered off.
It was extracted in a Soxhlet apparatus with chloroform. The
muddy yellow precipitate was filtered off and the

106. Gilman and Robinson, J. Am. Chem. Soc., 50, 1714 (1928).

tridodecyllead chloride was obtained by partial evaporation of the filtrate. It was recrystallized from ethyl acetate, then from petroleum ether (D). The product melted at 64-65°. A mixture of this and the product previously obtained melted at 63-64°.

2. Tridodecyllead nitrate.-- One and eighty-eight hundredths grams of tridodecyllead chloride and 0.43 g. of silver nitrate were refluxed with 50 cc. of absolute alcohol for an hour. The precipitated silver chloride was filtered off and the tridodecyllead nitrate was precipitated from the filtrate by the addition of water. The crude yield was 1.48 g.; m.p. 41-42°. Two recrystallizations from ethyl acetate raised the melting point to 44-45°.

Anal. Calc'd for $C_{36}H_{75}O_3NPb$: Pb, 26.66%. Found: Pb, 26.98%.

3. Tridodecyllead acetate.-- Two and one-quarter grams of tridodecyllead chloride were refluxed with 0.51 g. of silver acetate in 35 cc. of 95% alcohol for one-half hour. The residue was filtered hot; the R_3PbOAc crystallized readily on cooling. The yield was 1.65 g. (71%) of a product melting at 59°.

Anal. Calc'd for $C_{14}H_{28}O_2Pb$: Pb, 26.76%. Found Pb, 26.90%.

4. Tritetradecyllead chloride.-- Twenty grams of tetradecyl bromide (0.0722 mole) in 20 cc. of ether was added

slowly to 1.76 g. of magnesium in 80 cc. of ether. The Grignard solution was transferred as usual, and titrated. The normality was 0.545, and the volume was about 120 cc.; so the yield was 90.8% of the theoretical.

To the remaining 115 cc. of solution was added 7.59 g. of lead chloride. The solution darkened at once, and became red-brown. In fifteen minutes the color test was very weak. It was stirred and refluxed for six hours, then left to stand overnight. It was hydrolyzed by pouring into ice and 15 g. of ammonium chloride, and the ether was evaporated. The solid was filtered off and dried. It was partly black (lead) and partly a yellow solid; the characteristic organo-lead odor was noticeable.

It was treated with 75 cc. of hot chloroform, and filtered hot. The filtrate yielded some precipitate on cooling; this was filtered off, but it filtered very slowly. More was obtained by the addition of absolute alcohol to the filtrate. The two precipitates weighed 7.4 g., and melted respectively at 72-75° and 71-74°. They were combined and recrystallized from 150 cc. of hot petroleum ether (B); this removed a yellow insoluble solid which may have been R_3Pb; it was not investigated further. The filtrate on cooling yielded a white powder melting at 73-75°. It was recrystallized once more from ethyl acetate, and melted at 74-75°. Qualitative tests (107)

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107. Kamm, "Qualitative Organic Analysis," John Wiley and Sons, New York. (1932) p. 135.

showed it to contain lead and a trace of halogen, which proved to be chlorine.

Anal. Calc'd for $C_{42}H_{87}PbCl$: Pb, 24.8%; Cl, 4.25%. Found: Pb, 24.8%; Cl, 2.48%.

The chlorine analysis was carried out by the ordinary Parr bomb procedure, which often gives low results with organometallic compounds (see tetradecylmercuric bromide above).

5. Attempt to prepare trihexadecyllead bromide.-- Fifteen and one-quarter grams of hexadecyl bromide (0.05 mole) in 15 cc. of ether was added slowly to 1.22 g. of magnesium in 35 cc. of ether. The Grignard reagent was transferred as usual, and titrated. The normality was found to be 0.405, and the volume was estimated to be 91 cc., so the yield was 73.5% of theoretical.

To the remaining 86 cc. of the solution was added 8.5 g. of lead bromide. The mixture became black at once; the supernatant liquid was reddish, but the solid was black. It was stirred for one-half hour and let stand overnight. The product was hydrolyzed and the ether was evaporated. The residue was filtered and washed with water. When it was dried in air it weighed 14.0 g. It was extracted with hot ethyl acetate. The first precipitate from the filtrate was a yellowish solid melting about 50-55°, and weighing 6.8 g. It was recrystallized from chloroform, ethyl acetate, petroleum ether, and ethyl acetate; the final melting point was 66-69°.

<u>Anal</u>. Calc'd for $C_{48}H_{99}PbBr$: Pb, 21.51%. Found: Pb, 20.38%. Apparently the product was impure.

6. <u>Trihexadecyllead chloride</u>.-- Twenty-six and one-tenth grams of <u>n</u>-hexadecyl chloride (0.1 mole) and 2.43 g. of magnesium were refluxed with 125 cc. of dry ether for forty-five hours. The reaction was started by the addition of a few drops of propyl iodide. The yield of hexadecylmagnesium chloride was 92% of the theoretical.

To this solution was added 16.1 g. of lead chloride. The mixture was stirred and refluxed for eight hours, then set aside overnight. It was hydrolyzed with water and ammonium chloride. The ether was removed and the solids were filtered, washed, and dried. They were extracted in a Soxhlet apparatus with chloroform. The chloroform suspension was filtered to remove a fine yellow precipitate, and the filtrate was concentrated to give a nearly white precipitate of tricetyllead chloride. The crude yield was 14.0 g. (52.5%), melting at 77-79°. It was recrystallized from ethyl acetate and finally from petroleum ether (D). The pure product melted at 79-80°.

<u>Anal</u>. Calc'd for $C_{48}H_{99}PbCl$: Pb, 22.55%. Found: Pb, 22.67%.

7. <u>Trioctadecyllead chloride</u>.-- Twenty grams of octadecyl bromide (0.06 mole) in 30 cc. of ether was added slowly to 1.46 g. of magnesium in 70 cc. of ether. The Grignard reagent was filtered as usual. The coupling product, hexatriacontane,

is not very soluble in ether, and much of it remained behind in this filtration. The hexatriacontane was washed free of Grignard reagent with 50 cc. of ether.

To the Grignard reagent was added 10 g. of lead chloride (0.036 mole); the usual darkening and slight refluxing occurred. It was stirred at room temperature for eight hours, then refluxed for one-half hour before hydrolysis. After the ether had been removed, the solid was filtered and washed with water and alcohol. It weighed 22.9 g. It was extracted with hot ethyl acetate, leaving 6.5 g. of insoluble material, probably lead, and lead chloride or bromide. The filtrate on cooling yielded 13.7 g. (75.8%) of the crude yellowish compound, melting at about 60°. It was recrystallized four times from ethyl acetate and three times from petroleum ether (B) to yield trioctadecyllead chloride melting at $82-83^\circ$; the yield was only 2.0 g.

Anal. Calc'd for $C_{54}H_{111}PbCl$: Pb, 20.66%. Found: Pb, 20.71%

D. Organolead compounds--Tetraalkyllead types.

1. Attempt to prepare tetradodecyllead.-- Fifteen cubic centimeters of 0.781 N n-dodecylmagnesium bromide, and 50 cc. of ether, and 5.8 g. (0.0077 mole) of tridodecyllead chloride were refluxed for four hours. The product was hydrolyzed, the ether was evaporated, and the suspension was cooled. The solid was filtered off quickly and dissolved in ethyl acetate at

room temperature. The mixture was filtered to remove R_3PbCl and tetracosane. The filtrate was diluted with a little alcohol and cooled in ice. The precipitate was filtered off and recrystallized once from ethyl acetate, then from ether and alcohol, then from ethyl acetate and alcohol. The adsorbed solvents were removed in vacuo. The yield was 2.3 g. (33.7%) of impure tetradodecyllead melting at 18° to a cloudy liquid which became clear at about 29°.

Anal. Calc'd for $C_{48}H_{100}Pb$: Pb, 23.44%. Found: Pb, 22.19%.

Several attempts to purify the compound failed to yield pure tetradodecyllead.

2. Tetratetradecyllead.-- To 113 cc. of 0.664 N n-tetradecylmagnesium bromide was added 9.1 g. of lead chloride (0.0326 mole). This was stirred and refluxed for six hours, then allowed to stand overnight. It was hydrolyzed and the ether was removed by evaporation. The residue was filtered and dried, then extracted with chloroform. The chloroform solution was filtered to remove the usual yellow precipitate, then the chloroform was distilled off. The residue was suspended in ether and the solution was saturated with hydrogen chloride. After several hours the heavy white precipitate of tritetradecyllead chloride was filtered off. The original crude product weighed 10.4 g. (76.7%) and melted at $68-70^o$. It was recrystallized from petroleum ether (D) to yield 6.2 g.

(45.5%) of nearly pure R_3PbCl melting at 72°.

Six and two-tenths grams of n-tetradecyl bromide (0.0224 mole) was added to 0.55 g. of magnesium in 20 cc. of ether. Twenty-five cubic centimeters of the resulting 0.332 N Grignard reagent was added to 6.2 g. of tritetradecyllead chloride. The mixture was refluxed for seven hours, then hydrolyzed with aqueous ammonium chloride. The layers were separated and the ether layer was dried over sodium sulfate. It was cooled in ice to yield a heavy white precipitate. This was recrystallized from ethyl acetate, then from ether, to yield a small amount of low-melting white solid. The adsorbed solvent was removed in vacuo. The product melted at 31°.

Anal. Calc'd for $C_{56}H_{116}Pb$: Pb, 20.78%. Found: Pb, 20.92%.

From the filtrates the bulk of the tetratetradecyllead was recovered. There appeared to be comparatively little octacosane and tritetradecyllead chloride in the mixture.

3. Tetrahexadecyllead.-- Ten cubic centimeters of an ethereal solution containing 0.00482 mole of hexadecylmagnesium bromide was added to a suspension of 4.4 g. (0.00479 mole) of trihexadecyllead chloride in 50 cc. of ether. After eleven hours this was hydrolyzed, the ether was evaporated, and the product was filtered and dried. The dotriacontane was removed by being allowed to crystallize from ethyl acetate.

The filtrate from this was diluted with methanol to give impure tetrahexadecyllead, melting at about 43°. This was dissolved in ether at room temperature; the dotriacontane was again filtered off, and the R_4Pb precipitated by addition of alcohol to the filtrate. It was again recrystallized from ethyl acetate; the $C_{32}H_{66}$ was removed first at 33°; then the product was precipitated by methanol. It now melted at 42-43°, but did not become entirely clear until 60°. To remove the trihexadecyllead chloride, the product was suspended in petroleum ether (A), cooled in ice and filtered, and the filtrate was treated with methanol and ethyl acetate to obtain tetrahexadecyllead melting at 39-42°. It was recrystallized from ether. The melting point was 42°. The yield was 1.27 g., or 23.9% of theoretical.

Anal. Calc'd for $C_{64}H_{132}Pb$: Pb, 18.68%. Found: Pb, 18.56%.

Table 3

Melting Points of Organolead Compounds

R	$n\text{-}C_{12}H_{25}$	$n\text{-}C_{14}H_{29}$	$n\text{-}C_{16}H_{33}$	$n\text{-}C_{18}H_{37}$
R_4Pb	---	31°	42°	---
R_3PbCl	64-65°	74-75	79-80	82-83
R_3PbNO_3	44-45	---	---	---
$R_3PbC_2H_3O_2$	59	---	---	---

E. Organotin compounds--Tetraalkyltin types.

1. Tetradodecyltin.-- To 64 cc. of a 0.843 N solution of n-dodecylmagnesium bromide (0.054 mole), was added 4.7 g. (0.018 mole) of stannic chloride in 15 cc. of benzene. The mixture was refluxed for three and one-half hours, then hydrolyzed, and the ether was allowed to evaporate.

The residue was crystallized from ethyl acetate to give 5.4 g. (45%) of crude material. The tetracosane was removed by repeated recrystallization, leaving tetradodecyltin in the filtrates. The solvents were distilled off and the residue was recrystallized from ether and ethyl acetate, twice. The resulting product was dried in vacuo and filtered to remove a little solid. The filtrate was nearly pure tetradodecyltin, melting at 15-16° to a turbid liquid which was clear at 21°.

n_D^{30} 1.4692; n_D^{24} 1.4719; $n_D^{16.3}$ 1.4748; n_D^{20} 1.4736.

Anal. (108) Calc'd for $C_{48}H_{100}Sn$: Sn, 14.91%. Found: Sn, 15.18%.

2. Tetratetradecyltin.-- Twenty-seven and seven-tenths grams of n-tetradecyl bromide (0.1 mole) in 20 cc. of ether was added slowly to 2.43 g. of magnesium in 80 cc. of ether. The resulting Grignard reagent had a volume of 155 cc. and a

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108. Gilman and King, J. Am. Chem. Soc., 51, 1213 (1929). The use of bromine is not necessary with these non-volatile compounds.

normality of 0.563; so the yield was 87.2% of the theoretical.

To this was added 5.5 g. of liquid stannic chloride, slowly. The mixture was refluxed for one hour and then allowed to stand overnight. It was hydrolyzed, and the ether was removed by evaporation. The residue was treated with ethyl acetate at room temperature to dissolve out the tin compound and leave the octacosane; 1.7 g. of the latter was obtained thus, and a filtrate which on cooling yielded 12.7 g. (66%) of crude tetratetradecyltin, melting at 33-60°. It was recrystallized as before from ethyl acetate, and yielded a product melting at 33-37°. A third recrystallization gave 8.6 g. of tetratetradecyltin, melting at 33-34°.

Anal. Calc'd for $C_{56}H_{116}Sn$: Sn, 13.07%. Found: Sn, 12.92%.

3. Tetrahexadecyltin.-- To 102 cc. of 0.378 N n-hexadecyl-magnesium bromide was added 2.5 g. of stannic chloride dissolved in 20 cc. of benzene. After ninety minutes the mixture was poured into water and ammonium chloride. The ether was removed by evaporation, and the solid was filtered off and washed with water and alcohol. The dotriacontane was removed by dissolving the product in ethyl acetate, cooling to room temperature, and filtering. The filtrate was diluted with alcohol and cooled in ice, to yield 7.5 g. (76%) of crude tetrahexadecyltin, melting at 36-41°. It was recrystallized from ether twice to give pure tetrahexadecyltin, melting at 41.5-42.5°.

Anal. Calc'd for $C_{64}H_{132}Sn$: Sn, 11.63%. Found: Sn, 11.84%.

4. Tetraoctadecyltin.-- Fourteen and eight-tenths grams of n-octadecyl bromide (0.0445 mole) in 15 cc. of ether was added slowly to 1.08 g. of magnesium in 30 cc. of ether. The Grignard reagent was transferred and diluted to 100 cc. It was found by titration to be 0.390 N; so the yield was 87.6% of the theoretical.

To the remaining 90 cc. of solution was added 2.26 g. of stannic chloride (0.0087 mole), dropwise. After two hours of stirring and refluxing, the mixture was hydrolyzed and the ether was removed. The residue was filtered, washed with water, and dried. It weighed 9.4 g. and melted gradually at about 46°. It was recrystallized three times from ethyl acetate to give pure tetraoctadecyltin melting at 47°. The yield was 5.6 g. (56.8%).

Anal. Calc'd for $C_{72}H_{148}Sn$: Sn, 10.48%. Found: Sn, 10.36%.

F. Organotin compounds--Trialkyltin salts.

1. Tridodecyltin chloride.-- An ethereal solution of crude recovered tetradodecyltin was saturated with dry hydrogen chloride; the tube was then stoppered and set aside overnight. The ether was distilled off, and the residue recrystallized from ethyl acetate and methanol, by cooling overnight in the

icebox. It was recrystallized a second time from ethyl acetate and methanol, and again from ether-ethanol. The melting point was 33°.

Anal. Calc'd for $C_{36}H_{75}SnCl$: Sn, 17.93%. Found: Sn, 17.73%.

2. Tritetradecyltin chloride.-- An attempt to cleave tetratetradecyltin in petroleum ether (A) with dry hydrogen chloride gave only unchanged R_4Sn. Another attempt to cleave this tin compound with stannic chloride in benzene gave unreacted R_4Sn.

Cleavage of 3.6 g. of tetratetradecyltin in dry ether with dry hydrogen chloride gave, after standing for six hours, 2.6 g. (85%) of tritetradecyltin chloride, melting at $46-47^\circ$. Recrystallization from ethyl acetate did not change the melting point.

Anal. Calc'd for $C_{42}H_{87}SnCl$: Sn, 15.91%. Found: Sn, 15.29%.

3. Trihexadecyltin chloride.-- Two and one-tenth grams of tetrahexadecyltin (0.002 mole) was dissolved in dry ether, and the solution was saturated with dry hydrogen chloride at room temperature. The mixture was set aside overnight, then cooled, filtered, and washed. The product was crystallized from ethyl acetate. The yield was 1.27 g. (74%) of trihexadecyltin chloride, melting at $55.5-56.5^\circ$.

Anal. Calc'd for $C_{48}H_{99}ClSn$: Sn, 14.30%. Found: Sn, 14.75%.

4. <u>Trioctadecyltin chloride</u>.-- Two and two-tenths grams of tetraoctadecyltin (0.00194 mole) was dissolved in dry ether and saturated with hydrogen chloride. It was set aside over-night, and then worked up as usual. It was recrystallized from ethyl acetate, then from ether. The yield was 1.1 g. (62%) of trioctadecyltin chloride, melting at 61-62°.

<u>Anal</u>. Calc'd for $C_{54}H_{111}ClSn$: Sn, 12.98%. Found: Sn, 12.86%.

Table 4

Melting Points of Organotin Compounds

R	$\underline{n}-C_{12}H_{25}$	$\underline{n}-C_{14}H_{29}$	$\underline{n}-C_{16}H_{33}$	$\underline{n}-C_{18}H_{37}$
Tetraalkyltin	15-16°	33-34°	41.5-42.5°	47°
Trialkyltin chloride	33	46-47	55.5-56.5	61-62

G. <u>Organoarsenic compounds</u>.

1. <u>Tridodecylarsenic</u>.-- Twenty and one-half grams of <u>n</u>-dodecyl bromide (0.0822 mole) in 20 cc. of ether was added slowly to 2.0 g. of magnesium in 60 cc. of ether. The Grignard reagent was transferred as usual.

It was then cooled in water to 25° and a solution of 7.85 g. of arsenic tribromide (0.0249 mole) in 20 cc. of dry ether was added slowly. Two liquid layers separated, the upper brown, the lower, colorless. On standing overnight both layers became

dark. It was hydrolyzed with 4.5 g. of ammonium chloride in 18 cc. of water after standing twenty-four hours. The dark material settled out, leaving a white, turbid upper layer of liquid, and a smaller dark lower layer of liquid. Sodium sulfate was added to dry the ether layer. The upper layer was found to be free of halide when tested with silver nitrate and nitric acid.

The ether solution was filtered through dry asbestos under nitrogen; the filtrate was clear and colorless. The ether was distilled off in a stream of dry nitrogen; then dry nitrogen was passed through the heated oil overnight to remove the last traces of ether. If this is not done the material froths very badly in the subsequent distillation.

It was then distilled in an all-glass apparatus by means of a mercury vapor pump. The first fraction was taken up to 150° at 0.0004 mm. The next fraction, tetracosane, distilled a little higher than this, and solidified quickly in the receiver, from which it was removed by being melted. The last fraction was tridodecylarsenic, boiling at about 220° at 0.08 mm., or 200° at 0.009 mm., with the bath at 308°. The distillate was slightly cloudy, and slightly yellow. The yield was 8.12 g. (56% of the theoretical).

It was analyzed for arsenic by the method of Tabern and Shellberg (97).

Anal. Calc'd for $C_{36}H_{75}As$: As, 12.85%. Found: As, 12.41%.

A small glass bulb was weighed, filled with water at 20° to a mark, then was dried and reweighed, and inverted in the sample of R_3As. The whole was placed in a vacuum desiccator and evacuated; then when the air was readmitted, the bulb was filled with the R_3As. It was leveled off to the mark at 35° (since at 20° the compound was solid) by means of a very fine capillary. With the viscous oil this operation was rather difficult. A centrifuge helped greatly to remove the air bubbles which inevitably formed. The density, d_{20}^{35}, was 0.900. The refractive index (Abbe), n_D^{35}, was 1.4740.

From this the specific refraction was calculated to be 0.3098, and the molecular refraction 180.6. The value calculated for $C_{36}H_{75}As$ is 181.51 (value for arsenic from Jones et al. (81)).

2. Tritetradecylarsenic.-- Twenty-two and one-tenth grams of tetradecyl bromide (0.0797 mole) in 20 cc. of ether was added slowly to 1.94 g. of magnesium in 60 cc. of ether. The Grignard was transferred as usual. It was cooled externally, and a solution of 7.53 g. of arsenic tribromide (0.0239 mole) in 20 cc. of dry ether was added slowly. After three hours it was hydrolyzed with 4.5 g. of ammonium chloride in 17.2 cc. of water; then 14 g. of anhydrous sodium sulfate was added, and the mixture was allowed to stand overnight. It was filtered through asbestos under nitrogen; the filtrate was slightly cloudy. The ether was removed in a current of dry nitrogen, as before.

The residue was distilled at low pressure. Tetradecane boiled off at 70° at 0.22 mm. Octacosane, which solidified in the receiver, came over at $150-160^{\circ}$ at 0.0008 mm. This was removed and the temperature was raised slowly. There was slight fuming, then there was a sudden rapid distillation of liquid and a deposition of a black solid on the neck of the Claisen flask. The boiling point could not be raised over 180°, with the pressure fluctuating from 0.5 to 0.01 mm. at various times. After the bath had reached 310° and about half of the liquid had distilled, distillation was stopped. The distillate weighed 5.9 g., and the residue 4.6 g.

<u>Anal</u>. Calc'd for $C_{42}H_{87}As$: As, 11.22%. Found: for distillate, As, 8.6%; for residue, As, 11.19%.

The density and the refractive index of the residue were measured as described for tridodecylarsenic: d_{20}^{35} 0.908; n_D^{35} 1.4740. The specific refraction is therefore 0.3094, the molecular refraction 206.4. The calculated refraction for $C_{42}H_{87}As$ is 209.26.

A second preparation of tritetradecylarsenic was made using arsenious oxide (80) in place of arsenic tribromide. Eighteen and one-half grams of tetradecyl bromide in 20 cc. of ether was added slowly to 1.62 g. of magnesium in 50 cc. of ether. The reagent was transferred as usual. To this was added 1.98 g. of pure arsenic trioxide. Strong refluxing occurred. It was heated and stirred for one hour, then let stand for eleven hours. A color test number I (38) was

negative. The solution bleached iodine in acetic acid readily, indicating that trivalent arsenic was in the solution. The mixture was colorless, with a white precipitate. It was hydrolyzed with 3.7 g. of ammonium chloride in 15 cc. of water; twelve grams of sodium sulfate and 50 cc. of ether were added and the mixture was allowed to stand for several hours. It was filtered through asbestos under nitrogen. The ether was removed from the filtrate as before. When vacuum distillation was attempted, the tetradecane and part of the octacosane distilled, but the arsenical apparently decomposed, and the residue frothed so badly that distillation of the remaining hydrocarbon was impossible.

H. Organolithium compounds.

1. Introduction.-- Thirty runs of long-chained lithium compounds were made in all. Success was achieved in all of the solvents tried, under what were found to be proper conditions for the solvent. The alkyl chlorides reacted notably better than the bromides. No iodides were tried, since they had been shown to be unsatisfactory with the lower homologs (2).

In diethyl ether the reaction between lithium and the alkyl halides took place very readily with either the chlorides or the bromides; steady refluxing continued as long as the halide solution was added. The yields, as measured by simple

acid-base titration, varied considerably. Since other fac-
tors were controlled as carefully as possible, this is prob-
ably attributable to differences in the purity of the halides,
particularly the bromides. L. D. Green (109) claimed that
freshly distilled n-dodecyl bromide gave good yields of
dodecyllithium but that the same lot, on standing, gave poorer
results. Few runs with chlorides were made in ether, but
they were uniformly satisfactory. Unfortunately the greater
part of this work was done before the great need for the
double titration method of analysis was clearly understood;
so most of the results are of single titrations only.

In low-boiling petroleum ether (A), the reaction was slow
and required continuous external heating. The bromides tried
gave no results even on prolonged heating and with the use of
various methods of starting the reaction. The chlorides give
poorer yields than in ether. There was a very noticeable
difference between the single and double titration results,
even on the clear filtered solutions.

In ordinary petroleum ether (B), it was found best to
boil the solvent and the lithium first, then to add the
alkyl halide and to continue refluxing rapidly. No stirring
was required. The reaction was complete in about an hour,
during which time the lithium metal gradually sank to the
bottom of the flask. The yields with long-chained chlorides

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109. L. D. Green, unpublished work.

were better than in low-boiling petroleum ether, and the preparation took only about 2% of the time required in the latter case. A single trial run with n-dodecyl bromide showed that halide to be much less satisfactory than n-dodecyl chloride. Considerable differences were observed between the single and double titration results. No advantage was observed in mixing high- or low-boiling petroleum ether with the middle fraction.

In benzene, dodecyl chloride was much superior to dodecyl bromide for the preparation of dodecyllithium. The method of preparation was similar to that used with ordinary petroleum ether (B), and the results were about the same. Toluene was not as good a solvent for the preparation of dodecyllithium. No metalation of either benzene or toluene was observed.

It was not found possible to check the titration values by isolation of the acid obtained by carbonation by pouring the mixture jetwise into ether and dry ice. The yield of acid was generally much lower than the titration value, and the ketones formed (18) were not sufficiently easy to separate from the coupling products to give quantitative results.

Iodimetric titration was tried on one run of dodecyllithium in ordinary (60-68°) petroleum ether. The results were not encouraging; the iodine value was roughly equal to the single titration value.

In the few cases in which the "coupling and disproportionation"* products were separated after carbonation of the mixture, a markedly lower yield of "disproportionation" products (e.g., dodecane and dodecene from dodecyl chloride) was observed than in the preparation of alkylsodium compounds.

A single run of amyllithium in ordinary petroleum ether (60-68°) was made, in which the technique described for the long-chained compounds was employed. The good yield (72.7%) of amyllithium indicated that the method should be useful for short chains as well as for the longer ones.

Unless otherwise stated, unsaturate-free petroleum ether was used.

2. Preparation in ether.-- The procedure in all cases was entirely analogous to that used for the short-chained lithium compounds. The dried 250 cc. three-necked flask and condenser were swept out with nitrogen as usual. Ether was added, and the weighed amount of lithium was first hammered out flat, then cut with scissors into strips and dropped directly into the ether. The ether solution of the long-chained halide was then added slowly. After a little had been added the flask was warmed if necessary to start the reaction. When the characteristic slight turbidity (or a color test) indicated that some RLi had formed, the rest of the halide solution was dropped in slowly; the mixture generally refluxed gently. Stirring was employed at this stage

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*So called because they are assumed to arise from coupling and disproportionation of the free alkyl radicals.

only. The mixture was usually heated to reflux for about
15 to 30 minutes after spontaneous refluxing had ceased.

After the fine solids had settled somewhat, the mixture
was filtered under nitrogen through a dry asbestos pad. A
modification of the filtration apparatus previously de-
scribed (23) was used. The filtrate was usually not entirely
clear.

Table 5

Organolithium Compounds in Ethyl Ether.

No.:	Alkyl halide	RX moles	Li atoms	Ether cc.	Yield RLi, single ti-tration	Yield RLi, double ti-tration
(1)	octadecyl bromide	0.05	0.10	50	18.4%	---
(2)	octadecyl bromide	0.033	0.13	65	56.1	---
(3)	tetradecyl bromide	0.05	0.20	100	64.0	---
(4)	dodecyl bromide	0.05	0.20	100	65.1	---
(5)	dodecyl bromide	0.05	0.17	100	47.8	---
(6)	hexadecyl chloride	0.042	0.13	91	113	---(a)
(7)	dodecyl chloride	0.05	0.2	60	104.8	76.6(b)

(a) On carbonation, a 50.7% yield of margaric acid was ob-
tained, and a non-acidic, solid residue, which if assumed to
be dotriacontane, accounted for 53.9% of the halide used. Un-
doubtedly, however, this residue also contained dicetyl ketone,
as later experiments have shown.

(b) The single-titration yield did not vary much with time,
but the double-titration values were 76.6% after one hour,
41.4% after 53 hours, and 0% after 143 hours.

3. <u>Preparation in low-boiling petroleum ether</u> $(30-35^{o})$.--
Four unseccessful attempts to prepare long-chained lithium
compounds in low-boiling petroleum ether, from alkyl bromides
and lithium metal, were made before it was discovered that
alkyl chlorides gave positive results. A few drops of
n-butyl bromide were used to start the reaction in each case.
The long-chained chloride was then added rapidly, and the
mixture was refluxed for several days. The average yield of
dodecyllithium was 46.1%, while a single reliable run of
hexadecyllithium gave a 44.5% yield; the results varied
widely, and no conclusions concerning the effect of chain
length on the yield can be drawn. The procedure was essen-
tially that described by Gilman, Langham, and Moore (23).

Table 6

Organolithium Compounds in Low-boiling Petroleum Ether.

No.	Alkyl halide	RX Moles	Li Atoms	Sol-vent in cc.	Time in hrs.	% Yield of RLi Single titra-tion	Double titra-tion
(1)	n-Dodecyl bromide	0.05	0.20	100	24	trace	---
(2)	n-Dodecyl bromide	0.05	0.10	50	15	0	---
(3)	n-Tetradecyl bromide	0.05	0.11	50	6	0	---
(4)	n-Dodecyl bromide	0.05	0.20	100	160	0	---
(5)	n-Dodecyl chloride	0.05	0.20	60	2	7.2	---
(6)	n-Dodecyl chloride	0.05	0.29	100	69	72	57.2
(7)	n-Hexadecyl chloride	0.05	0.30	100	172	44.5	5.4
(8)	n-Dodecyl chloride	0.05	0.30	60	53	71	35
(9)	n-Hexadecyl chloride	0.05	0.30	100	264	63.1	44.5

Notes on table:

(1) A weakly positive color test number I (38) was obtained, and a slight (ca. 2%) single-titration value.

(2) Dodecyl iodide, iodine, and a small amount (0.05 mole) of ether were added, but the reaction failed to start.

(3) Butyl bromide was added to form a small amount of n-butyllithium. The n-tetradecyl bromide was added and the mixture was refluxed. There was no evidence of further reaction. The color test finally became negative.

(4) A small amount of a previously prepared solution of dodecyllithium in high-boiling petroleum ether (D) was added. On refluxing the mixture the color test gradually changed from weakly positive to negative.

(5) The surface of the lithium became coppery in color about ten minutes after the first of the dodecyl chloride had been added. The solution became slightly turbid. When the external heat was removed and more chloride was added, no spontaneous refluxing occurred. A color test number I was faintly positive in fifteen minutes. The rest of the chloride was added slowly, with stirring and heating. The solution was filtered through asbestos; the filtrate was turbid, and slightly pink in color. Single titration with N/10 sulfuric acid showed the normality to be 0.09. In titrations in petroleum ether and in benzene, the addition of alcohol greatly hastens the diffusion of lithium from the organic to the aqueous layer, and enables the titration to be carried

out rapidly. The volume of the filtrate was 40 cc.; the yield
was therefore 0.0036 mole. A color test number I was strongly
positive.

(6) A few drops of n-butyl bromide were added to start
the reaction. The n-dodecyl chloride was then added all at
once. After fifteen hours a color test number I was strongly
positive. The suspension was blue-violet and the supernatant
liquid was almost colorless. No stirring was employed after
the first one and one-half hours. After forty-eight hours of
refluxing, the lithium had sunk to the bottom--a phenomenon
always observed in the preparation of alkyllithium compounds
in petroleum ether. Refluxing was stopped after fifty-three
hours and the mixture was allowed to settle overnight. It
was then filtered under nitrogen through an asbestos pad. The
first part of the filtrate was very turbid and white; the
blue precipitate then filtered out and packed the filter so
that the latter half of the filtration was very slow, but the
filtrate was entirely clear and colorless. The filtrate was
shaken before samples were taken. Ether was added to the
benzyl chloride in the second titration; otherwise the reaction
between benzyl chloride and dodecyllithium is very slow. The
normality by simple titration was 0.381; by double titration
it was 0.301. Color tests number I and IV (110) were both
positive.

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110. L. Woods has found that benzylamine in petroleum ether
     gives a red color with reactive organometallic compounds;
     this has been called color test number IV (unpublished
     work).

(7) The operation was similar to that described in experiment (6). Simple titrations were carried out at various time intervals; the values are shown in Table 7.

Table 7

Titration of Hexadecyllithium

No.	Time in hrs.	Normality	Volume in cc.	Yield in %
1	50	0.145	80	23.3
2	73	0.247	65	34.2
3	98	0.173	80	27.6
4	148	0.302	65	45.2
5	172	0.237	75	44.5

The solution was filtered and the filtrate titrated by the double titration method; the yield was found to be 5.4%, but no ether was added with the benzyl chloride, so the value was probably worthless. The remaining solution was carbonated by pouring into dry ice and petroleum ether (A). The mixture was hydrolyzed and acidified. A white solid melting at 83° separated; it was insoluble in water and petroleum ether. Recrystallization raised the melting point to $84-85^\circ$. This product was subsequently shown to be dihexadecyl ketone /experiment (9)7. An attempt was made to fractionate the other products by distillation, but the results were very unsatisfactory. The total yield of RLi was estimated to be 14-15% of the theoretical.

(8) Ordinary, undried, unpurified "Skelly A" was used

instead of the unsaturate-free solvent. The reaction was
started with a little n-butyl bromide. After titration the
solution was poured into dry ice and ether. There was ob-
tained, on working up the mixture, 2.2 g. (28%) of tetraco-
sane, 0.7 g. (9.1%) of dodecane, and 3.3 g. (36.2%) of tri-
decylic acid. The refractive index, n_D^{20}, of the dodecane
fraction was 1.4303, which indicated 59.5% of dodecane and
40.5% of dodecene in the mixture (see the section on the
dodecane obtained from dodecyl chloride and sodium, p. 82,
for justification of this method of estimation). No dido-
decyl ketone was observed in this case, but it may have been
present.

(9) The solution was carbonated by pouring into dry ice
and ether. It was worked up as usual. There was obtained
2.5 g. of white crystals, not soluble in petroleum ether (A)
or water, and melting at 80°; recrystallization raised this
to 86-87°. The oxime was prepared by the ordinary procedure
(111); it melted at 60°. These two products were probably
dihexadecyl ketone and its oxime; the yield of ketone (crude)
was 23.5%.

Anal. Calc'd for $C_{33}H_{67}ON$: N, 2.83%. Found: N, 3.33%.

The filtrates from the crystallization of this ketone
were dried and the solvents were distilled off. The residue
was distilled. There were obtained 1.4 g. (13.9%) of "cetane,"
3.3 g. (27.2%) of margaric acid, and 2.0 g. (20%) of residue,
largely dotriacontane. From this, the total yield of

111. Kamm, ref. 107, p. 170.

hexadecyllithium was about 50.5%, compared with the double titration value of 44.5%. Due to difficulty in separating the ketone from dotriacontane, this value is not accurate.

4. **Preparation in higher-boiling fractions of petroleum ether.**-- In the higher-boiling hydrocarbon solvents reaction took place readily at reflux temperature. No catalyst and no stirring were required. The yields were good only when chlorides were used.

Table 8

Organolithium Compounds in Petroleum Ether.

No.:	Alkyl halide	RX Moles	Li Atoms	Sol- vent	Sol- vent in cc.	Time in hrs.	Yield in %	
							Single titra- tion	Double titra- tion
(1)	n-Dodecyl bromide	0.05	0.10	D	35	12	0	--
(2)	n-Dodecyl chloride	0.05	0.30	B	50	1	86.2	74.6
(3)	n-Dodecyl chloride	0.05	0.30	B	50	1	81.3	61.4
(4)	n-Dodecyl bromide	0.05	0.30	B	50	5	33.6	15.8
(5)	n-Dodecyl chloride	0.05	0.30	A-B	50	3.5	81.3	57
(6)	n-Dodecyl chloride	0.05	0.30	B-D	50	1.5	77.8	56
(7)	n-Dodecyl chloride	0.05	0.30	B	40	1.5	80.3	55.8
(8)	n-Amyl chloride	0.05	0.30	B	50	1	86.8	72.7

Notes on table:

(1) The lithium and solvent were heated with part of the n-dodecyl bromide; then a little iodine was added and heating

was continued for a short time. The mixture was cooled to
room temperature and stirred. A color test number I was nega-
tive. The solution contained a heavy precipitate.

(2) The solvent was refluxed rapidly with lithium and a
small crystal of iodine for fifteen minutes; then the n-dodecyl
chloride was added quickly and refluxing was resumed. The
reaction started at once. A heavy bluish precipitate formed.
The lithium sank to the bottom within an hour. Heating was
stopped, and the mixture was allowed to settle. The super-
natant liquid was titrated one-half hour later.

(3) The conditions of the second experiment were dupli-
cated, but the addition of iodine was omitted. The reaction
again started at once, and the mixture became bluish within
five minutes. The temperature of the refluxing liquid was
$67-68^{\circ}$. Refluxing was continued for one hour.

(4) n-Dodecyl bromide was used under the conditions of
experiment (3). A white turbidity appeared quickly, but the
mixture did not become blue. Refluxing was continued for
five hours.

(5) The solvent was a mixture of 25 cc. of petroleum
ether (A) and 25 cc. of petroleum ether (B). The lithium and
solvent were heated for seven minutes before the n-dodecyl
chloride was added. The temperature of the refluxing liquid
was 49°. The reaction was much slower than in experiment (3).
The precipitate was red-brown at first, then red-violet, and
finally became similar to the blue precipitate usually obtained.

(6) A mixture of petroleum ethers (B and D) was used. The temperature of the refluxing liquid was 78.5°. The conditions otherwise, were the same as in experiment (5). The reaction was very rapid.

(7) The solvent was boiled with lithium and a small crystal of iodine for fifteen minutes; then the n-dodecyl chloride was added slowly, over a period of fifteen minutes. Refluxing was continued for an hour after this. No improvement in the yield due to slow addition of chloride was noted.

The solution was also titrated by adding 10 cc. aliquots to 25-cc. portions of 0.992 N iodine in benzene. The mixture became warm. The excess iodine was titrated with 0.830 N sodium thiosulfate. Three values were obtained:

    a) clear solution; 0.66 N

    b) turbid mixture; 0.73 N

    c) turbid mixture; added 2 cc. of glacial acetic acid

       and excess solid $NaHCO_3$ before titrating; 0.68 N

For comparison, the single-titration and double-titration values were 0.72 N and 0.50 N, respectively.

(8) n-Amyl chloride was employed under the conditions of the second experiment. Eastman Technical amyl chloride was used directly without purification; the solvent was unpurified "Skelly B." The mixture was refluxed for one hour. Titrations were carried out on the turbid and clear solutions; there was no significant difference in either the single or the double titration values that could be attributed to turbidity. The

turbidity is, therefore, due to a neutral substance, probably lithium chloride.

5. <u>Preparation in aromatic solvents</u>.-- Benzene was shown by Ziegler and Colonius (2) to be an excellent medium for the preparation of lithium compounds. n-Dodecyllithium is readily prepared in it, and does not metalate it.

Table 9

Dodecyllithium in Aromatic Solvents

No.	Alkyl halide	RX Moles	Li Atoms	Sol- vent	Sol- vent in cc.	Time in hrs.	Yield in % Single titra- tion	Double titra- tion
(1)	n-Dodecyl chloride	0.05	0.3	Benzene	50	15	83.4	67.8
(2)	n-Dodecyl chloride	0.05	0.3	Toluene	50	1	28.3	10.0
(3)	n-Dodecyl bromide	0.05	0.3	Benzene	50	1	36.9	23.5

<u>Notes on table</u>:

(1) The solvent was refluxed with the lithium, 0.5 cc. of n-butyl bromide, and a small crystal of iodine for an hour before the dodecyl chloride was added. Undoubtedly no catalysts at all would have been required, in view of the (later) experiments with petroleum ether. The mixture was refluxed gently for fifteen hours after the chloride was added.

The mixture was carbonated with dry ice as usual. The only acidic substance obtained was tridecylic acid. No trace

of benzoic acid could be found. The yield of tridecylic acid was 2.45 g. (23%). The non-acidic fraction was dissolved in petroleum ether (B) and cooled to 15°, then set aside at room temperature for several hours. The white precipitate was filtered off and washed; m.p. 73-74°. A portion of it was treated with hydroxylamine (111). The oxime obtained melted at 47-48°.

Anal. Calc'd for $C_{25}H_{51}ON$: N, 3.67%. Found: N, 3.58%.

Didodecyl ketone and its oxime have not been described in the literature, but the melting points of their neighboring homologs indicate that this was the product obtained by the carbonation of dodecyllithium.

(2) The toluene was refluxed with the lithium and a small crystal of iodine; then the n-dodecyl chloride was added. Refluxing was continued for one hour. The yield shown was obtained in this time; when the mixture was kept warm for twenty hours, the yield fell to 4%.

(3) The reaction was started as in the first experiment. The n-dodecyl bromide was added all at once; refluxing was continued for one hour.

6. Metalation with dodecyllithium.-- Five and four-tenths grams of 1,2,3-trimethoxybenzene (0.032 mole) was added to 105 cc. of 0.3 N dodecyllithium in petroleum ether (B). The mixture was allowed to stand for fifteen hours at room temperature, then was poured into dry ice and ether. The

product was hydrolyzed and acidified, and the aqueous layer was drained off. The ether solution was extracted with dilute aqueous $NaHCO_3$, which was acidified to yield a small quantity of a precipitate melting at 85-90°. It was recrystallized from ether and petroleum ether (A); m.p. 98-100°. 2,2,4-Trimethoxybenzoic acid melts at 99° (112).

Anal.: 0.1432 g. of acid required 5.98 cc. of 0.1048 N sodium hydroxide. Calc'd for $C_{10}H_{12}O_5$: Neut. equiv., 223. Found: Neut. equiv., 228.

The silver salt was made by the addition of silver nitrate to this neutral solution. It was dried, and refluxed with methyl iodide. The methyl ester could not be crystallized. The methyl ester of 2,3,4-trimethoxybenzoic acid is an oil (112).

I. Organosodium compounds.

The technique used by Morton and his co-workers (16, et al.) in the preparation of amylsodium was the basis for the experiments on long-chained sodium compounds.

To prepare sodium sand the weighed quantity of clean sodium under about 50-100 cc. of xylene in a 250 cc. Erlenmeyer flask was heated to approximately 110°. The flask was stoppered and shaken hard. Usually the coarse sand so obtained was re-heated to 110° and shaken again, in order to obtain finer

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112. Will, Ber., 21, 2020 (1888).

sand. The xylene was then poured off and the sand was washed
several times with the solvent to be used, then scraped into
more of this solvent contained in the nitrogen-filled three-
necked flask in which the reaction was to be carried out.

A small amount of n-amyl alcohol was added to this, and
the mixture was stirred until reaction had stopped, which
took about fifteen minutes. The flask was then cooled to the
desired temperature. A water or ice bath was generally used,
although an inert bath cooled with dry ice is much safer.

The alkyl halide dissolved in some of the solvent was
slowly added to the cooled, stirred mixture. Reaction gener-
ally started within fifteen minutes; the length of the induc-
tion period depended largely on the temperature. The start
of the reaction was marked by the darkening of the sodium.
The mixture subsequently turned brown and became a sludge.

In most cases the mixture was carbonated by pouring
directly into a mixture of dry ice and ether or petroleum
ether. In a few cases carbonation was effected by passing in
dry gaseous carbon dioxide. Titration with iodine in benzene
was also tried.

1. Hexadecylsodium.-- Hexadecyl chloride reacted with
sodium metal to give hexadecylsodium. The results are shown
in Table 10.

Table 10

Preparation of Hexadecylsodium

No.	RCl Moles	Sodium Atoms	Sol-vent (98)	Vol. in cc.	Temp. in °C.	Margaric acid (%)	Hexadecane and Hexa-decene (%)	Dotria-contane (%)
(1)	0.075	0.37	A	65	17-R*	18 (?)	11.8(?)	39 (?)
(2)	0.05	0.25	B	100	17-21	15.9	23.9	25.9
(3)	0.05	0.25	D	175	18-45	5.6	---	12.5(?)
(4)	0.05	0.25	C_6H_6	100	21-26	7.0	44.3	14.5
(5)	0.05	0.25	A	100	0-R	4.4	48.4	39.4
(6)	0.05	0.26	C_6H_6	110	16-19	---**	---	---

*In this and the following tables, R denotes room temperature.
**In this experiment the products were examined for benzoic acid.

Notes on tables:

(1) The RCl was added in one and one-half hours. The total time of reaction was three and one-half hours. The mixture was carbonated with dry ice. Alcohol was added to react with the excess sodium. The mixture was hydrolyzed and warmed; then the aqueous layer was filtered. The filtrate was acidified and 10 g. of impure margaric acid was obtained. This was found to contain a large proportion of dotriacontane, which was separated by crystallization from petroleum ether. The acid was determined by a combination of titration and isolation to be 18.1%. The value for hexadecane was obtained by difference, based on the original 10 g. of solid obtained.

(2) The total time was three hours. The mixture was carbonated with dry ice, decomposed with alcohol, and hydrolyzed. The cold suspension was filtered, the precipitate

was washed with petroleum ether, and heated with dilute hydro-
chloric acid to obtain crude margaric acid, m.p. 54-57°.
Margaric acid is reported to melt at 60-61° (113). The hydro-
carbons were recovered from the petroleum ether and separated
by distillation.

(3) The mixture was filtered after preparation was com-
plete. The filtrate gave no color test number I (38), and
5 cc. of it required but one drop of N/10 sulfuric acid to
make it acidic. The unfiltered portion was carbonated with
dry ice, and decomposed as usual. The insoluble sodium
margarate was filtered off and washed with petroleum ether.
It was then dissolved in warm water and the free acid was pre-
cipitated by the addition of HCl. The dotriacontane was re-
covered from the petroleum ether. The hexadecane fraction
was not isolated.

(4) The total time was nineteen hours; the time of addi-
tion was one and one-half hours. The mixture was carbonated
with dry ice, and subsequently decomposed with alcohol and
water. No benzoic acid was found in the aqueous solution.
The warm soap solution was filtered and the filtrate acidi-
fied to obtain 0.95 g. of crude margaric acid, m.p. 54-56°.
The hydrocarbon fraction was distilled to obtain hexadecane
and dotriacontane. (See Table 10.)

(5) The RCl was added at 0° in twenty-five minutes; then

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113. Le Sueur, J. Chem. Soc., 85, 827 (1904).

the mixture was allowed to warm to room temperature. The total time before carbonation was fourteen hours. The mixture was carbonated with dry ice. It was hydrolyzed carefully and acidified with HCl. The aqueous solution was extracted with petroleum ether, and the hydrocarbon layer was washed, dried over sodium sulfate, and distilled. The margaric acid melted, not sharply, above 53°. The cetane fraction boiled at from 178° at 45 mm. to 185° at 49 mm.; n_D^{20} 1.4383. The iodine number was determined by titration with Hanus solution to be 41.4. The iodine number calculated for hexadecene is 113. The proportion of hexadecene in the "cetane" fraction was thus 41.4/113 or 36.6%. The refractive index (n_D^{20}) of hexadecane is 1.4347; that of hexadedene-1 is 1.4441 (114). The proportion of hexadecene in the mixture based on the refractive index is 36/94 or 38.3%. The agreement is as good as can be expected.

(6) The total time was eighteen hours. The mixture was carbonated with dry ice and examined for benzoic acid. The basic aqueous solution was acidified with sulfuric acid and distilled with steam, but no benzoic acid could be found in the distillate; the sensitive ferric benzoate test (115) was negative. The residue was treated with calcium chloride to remove margaric acid, and filtered. The filtrate gave a

114. Doss, "Physical Constants of the Principal Hydrocarbons." The Texas Company, N. Y. (1939).

115. Fischer and Gruenert, Z. Untersuch. Nahr. u. Genussm., 17, 725 (1909).

precipitate which had a pleasant odor of ferric benzoate, when neutralized and treated with ferric nitrate solution. A small amount of acid, melting at 110-115°, was isolated. It was sublimed, but the melting point was unchanged. A mixed melting point with authentic benzoic acid (m.p. 121°) was 112-117°.

2. Dodecylsodium.-- n-Dodecyl chloride reacted with sodium metal at moderate temperatures to yield dodecylsodium, dodecene, dodecane, and tetracosane. Rapid carbonation converted the dodecylsodium to tridecylic acid; slow carbonation gave a mixture of tridecylic acid and undecylmalonic acid. The results are given in Table 11.

Table 11

Preparation of Dodecylsodium

No.	Halide	RX Moles	So-dium Atoms	Sol-vent	Vol. in cc.	Temp. in °C.	Total acids (%)	Dodecane and do-decene (%)	Tetra-cosane (%)
(1)	Bromide	0.05	0.22	D	100	R-65	trace	----	----
(2)	Chloride	0.086	0.374	A	150	0-4	17.9	46.5	22.0
(3)	"	0.086	0.374	A	150	0-re*10.9		24.2	25.6
(4)	"	0.086	0.374	A	150	R-re	14.7	49.9	27.4
(5)	"	0.0576	0.252	A	100	R-re	12.7	25.5	21.0
(6)	"	0.0576	0.252	A	100	0-R	8.5	16.3	6.3
(7)	"	0.0576	0.252	A	100	0-9	12.7	44.0	23.1
(8)	"	0.0576	0.252	A	100	14-R	8.2	59.8	15.5
(9)	"	0.0576	0.252	A	150	14-R	20.3	52.0	19.5
(10)	"	0.0576	0.252	Ether	125	0	0.9	71.5	10.3
(11)	"	0.05	0.252	A	100	15-R	----	31.8	----
(12)	"	0.05	0.274	Kero-sene	100	17-R	6.8	----	----
(13)	"	0.0576	0.265	Ben-zene	125	15-23	4 (a)	----	----
(14)	"	0.05	0.8	A	125	16-R	67 (b)	----	----
(15)	"	0.05	0.8	A	125	18-R	42.6	30.6	6.0
(16)	"	0.05	1.2	A	125	19-R	29.7	45.8	14.2

* In this table re indicates reflux.
(a) Benzoic acid
(b) Iodine titration

Notes on table:

(1) Color tests numbers I, II (116), and IV all indicated that some organosodium compound had formed. On carbonation, acidification, and extraction with ether a small amount of acidic material was recovered.

(2) The dodecyl chloride was added during forty minutes. After eight hours the mixture was carbonated with dry ice.

116. Gilman and Swiss, J. Am. Chem. Soc., 62, 1847 (1940).

After hydrolysis and acidification, the petroleum ether layer was washed with water and dried over sodium sulfate. The products were separated by distillation; after removal of the solvent, the dodecane and dodecene distilled at about 137° at 67 mm. Tridecylic acid was collected at 160-215° at 15 mm.; it melted at 35-40°. Tridecylic acid is reported to melt at 40-41° (117).

(3) The RCl was added in thirty minutes at 0°; then the reaction was continued at reflux temperature for one and one-half hours. The mixture was carbonated, and decomposed with 25 cc. of alcohol. The sodium tridecylate was filtered off and washed with petroleum ether. The sodium salt was then dissolved in warm water and filtered. The tridecylic acid (2.0 g.) was recovered from the filtrate by acidification. The hydrocarbons were distilled. The yield of dodecane was low, as was usually the case when this method of separation was used.

(4) The RCl was added in one and three-quarters hours. No cooling bath was used, and the mixture refluxed spontaneously after seventeen minutes from the start. It was carbonated after two and one-half hours. After hydrolysis and acidification the organic layer was dried and distilled. Dodecane was collected between 140° at 88 mm. and 140° at 15 mm; tridecylic acid was then taken up to 215° at 15 mm. Titration of the tetracosane fraction required only about 2 cc. of N/10

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117. Le Sueur, J. Chem. Soc., 87, 1888 (1905).

base, of the dodecane fraction about 6 cc. Thus none of the fractions was pure, but the errors tend to compensate one another, and the results are probably accurate within a small percentage.

(5) The RCl was added during one-half hour; the mixture was allowed to reflux spontaneously. After three and one-quarter hours dry gaseous carbon dioxide was bubbled through the mixture. After hydrolysis and acidification the products were separated by distillation. No acid insoluble in petroleum ether was noted.

(6) The RCl was added in one-half hour at 0°. The mixture was stirred for three and one-half hours after this, at from 0° to 25°; then it was carbonated with dry gaseous carbon dioxide. After hydrolysis and acidification there was a considerable amount of substance insoluble in the petroleum ether layer. This was separated, dissolved in aqueous KOH and reprecipitated with HCl. It melted at $106-107^{\circ}$ and weighed 0.1 gram. Undecylmalonic acid (118) melts at 108.5°. The other products were separated from the filtrate by distillation. The yield of undecylmalonic acid was 0.7%; that of tridecylic acid was 7.8%. Accidental losses accounted for the low recovery.

(7) The RCl was added in thirty-five minutes, and the mixture was stirred subsequently for eight hours, then

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118. Levene, West, Allen, and van der Scheer, *J. Biol. Chem.*, 23, 70 (1915).

carbonated with dry gaseous carbon dioxide. Undecylmalonic acid (1.5%), m.p. 103-104°, and tridecylic acid (11.5%) were obtained. The products were separated as in experiment (6). The "dodecane" fractions from experiments 2, 3, 4, 5, 6, and 7 were combined; n_D^{20} 1.4277. The refractive indices of dodecane and dodecene-1 are 1.4219 and 1.4360, respectively. From these figures the proportion of dodecene in the "dodecane" fraction was 58/141 or 41%. The iodine number (Hanus) of the mixture was found to be 53.5 and 54.2, in two determinations. The iodine number of dodecene was calculated to be 151. From this, the proportion of dodecene was 53.8/151 or 35.6%. The agreement is reasonably good. The iodine number of the n-dodecyl chloride was found to be 0.96.

(8) The RCl was added in forty-five minutes; then the mixture was stirred for two hours. It was allowed to settle and was then filtered. The filtrate gave a negative color test number I (38). It was distilled without further treatment. Dodecane was collected at 127° at 83 mm.; tetracosane was left in the distilling flask. The yield of dodecane was 2.8 g. (33%), n_D^{20} 1.4273; iodine number 55.0, 56.5, average 55.8. The percentage dodecene in the "dodecane" fraction was 37%, from the iodine number, or 38.3% from the refractive index. The mixture of sodium and dodecylsodium filtered off was carbonated with dry ice. The products were separated by distillation, after hydrolysis and acidification. The final total yields are shown in Table 11, number 8.

(9) The RCl was added in twenty minutes. The mixture was carbonated with dry ice two hours later. The products were separated by distillation, after hydrolysis and acidification.

(10) The RCl was added in fifty minutes; the mixture became black, then brown, and finally black again. It was carbonated with dry ice after a total of two and one-half hours. After hydrolysis the acidic materials were extracted with dilute sodium hydroxide solution, which was washed with ether, then acidified, and the acid extracted with ether. The ether solution was dried over sodium sulfate and evaporated. Titration of the soft residue required 4.75 cc. of 0.1048 N sodium hydroxide. The p-toluidide of the acid was prepared (119). It melted at 86°; the p-toluidide of tridecylic acid melts at 88°. The neutral fraction was then distilled. The "dodecane" weighed 7.0 g., and boiled at 129° at 63 mm. Its iodine number was 32.2, indicating 32.2/151 of 21.3% of dodecene. The refractive index, 1.4244, indicated 17.7% of dodecene in the "dodecane" fraction.

(11) The solvent recovered from this run showed no reaction with Hanus solution when 10 cc. was run through the iodine-number procedure.

(12) The RCl was added in one-half hour. After four and one-half hours the mixture was partially filtered, under nitrogen, through an asbestos pad. The filtrate was clear

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119. Kamm, l.c., p. 177.

and colorless, gave no color test number I with a 5 cc. sample; 5 cc. required one drop of N/10 acid to acidify, and gave no yellow-flame test. The residue was carbonated with dry ice. The mixture was hydrolyzed and acidified, and the kerosene layer was washed with water and titrated with N/10 sodium hydroxide.

(13) The RCl was added in fifteen minutes. The mixture was stirred for two more hours and allowed to stand overnight. It was carbonated eighteen and one-half hours after the start. The mixture was hydrolyzed and acidified, and the benzene layer was dried and distilled. The solid distillate was distilled with steam. On cooling the distillate, benzoic acid crystallized out; melting point and mixed melting point 121-122°. The residue from the steam distillation was washed with water, and combined with the distillate. The whole was neutralized carefully, and ferric nitrate solution was added. The flesh-colored ferric benzoate (115) was filtered, washed, and dried; it weighed 0.95 g., which represented a 4% yield of benzoic acid. The tridecylic acid was precipitated from the water-insoluble residue with calcium chloride and recovered. The yield was less than 0.1 g.; m.p. 39-40°.

(14) The RCl was added in one hour. After four hours the mixture was cooled in ice, and 75 cc. of 1.334 N iodine in benzene was added quickly. After five minutes the mixture was filtered rapidly with suction. The filtrate was titrated with 0.874 N thiosulfate. There was 72.34 cc. of the iodine

solution used up. Based on the equation

$$RNa + I_2 \longrightarrow RI + NaI$$
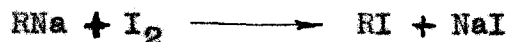
this indicated a 76% yield of dodecylsodium. A duplicate run showed a 67% yield of dodecylsodium; this is a more reliable value.

(15) The RCl was added in fifty minutes; then the mixture was stirred for three and one-half hours. It was hydrolyzed and acidified. The products were separated by distillation. The "dodecane" distilled at 125-130° at 58 mm.; n_D^{20} 1.4280; the proportion of dodecene was estimated from this to be 43.2%.

(16) The RCl was added in forty-five minutes; very little darkening was observed. Fifteen minutes later the mixture began to reflux, and turned brown. Refluxing lasted for about one minute. The mixture was carbonated with dry ice after a total of two hours. The refractive index of the "dodecane" fraction was 1.4285 at 20°; the proportion of dodecene in the "dodecane" fraction was estimated to be 46.8%.

3. Amylsodium.-- Amyl halides and sodium reacted to give amylsodium. The results are given in Table 12.

Table 12

Preparation of Amylsodium

No.	Halide	RX Moles	Sodium Atoms	Sol-vent	Vol. in cc.	Temp. °C.	Acids Caproic in %	Butyl-malonic in %	De-cane
(1)	n-Amyl br.*	0.13	0.65	A	66	0-R	21	----	----
(2)	" "	0.13	0.65	A	66	19-27	3.2	9.9	19.2
(3)	" "	0.13	0.65	D	66	R	0.1	8.1	30.9
(4)	n-Amyl ch.*	0.16	1.3	A	190	0-4	27.1	14.4	12.5
(5)	" "	0.05	0.25	A	125	17-R	34.7(a)	----	----
(6)	" "	0.05	0.25	A	125	16-R	36.3(a)	----	----
(7)	" "	0.05	0.38	A	36	0-reflux	52.4(a)	----	----

* In this table br indicates bromide and ch indicates chloride.
(a) Iodine titration

Notes on table:

(1) The RBr was added in one hour at 0°; the mixture was then stirred for two hours at room temperature, then carbonated with dry ice. After hydrolysis the basic solution was extracted with ether, then acidified, and again extracted with ether. The ether was dried and distilled off. The residue weighed 3.2 g. Calculated as caproic acid this was 0.0276 mole, or 21% of the theoretical. No separation of caproic and butylmalonic acids was attempted.

(2) The RBr was added at 19°; the mixture was carbonated with dry ice after five hours at room temperature. After hydrolysis the basic solution was washed with ether, then acidified and extracted with petroleum ether (B). The extract was dried over sodium sulfate, and the solvent was

distilled. The residue weighed 0.5 g. The aqueous solution was then extracted with ether; the ether was dried and removed as before. The residue was an oil weighing 2.1 g. Morton, Le Fevre, and Hechenbleikner (15) claimed that this method effected "95% separation" of the acids; they did not weigh the acids, but titrated them. The yield of decane was 3.6 g. (19.2%).

(3) The RBr was added in one and one-half hours at room temperature. Stirring was continued for a total of five and one-half hours. A color test number IV (110) was positive. The mixture was carbonated with dry ice. The acids were separated as in experiment (2). The yield of decane was 5.8 grams (30.9%).

(4) This was a duplicate of an experiment by Morton and Richardson (120). The amyl chloride was added in one-half hour at 0°. The sodium was black in five minutes. After the RCl was added the mixture was refluxed (35°) for two hours, then carbonated with dry ice. The acids were separated as in experiment (2). An aliquot of the caproic acid was titrated; the yield was 27.1%. The rest was treated to isolate the caproic acid; the yield on the basis of the crude acid obtained was 30.8%. The solution of butylmalonic acid was neutralized, and the acid precipitated and weighed as its cupric salt. The yield of copper butylmalonate was 5.55 g. The yield of dodecane was 2.8 g. (12.5%).

120. Morton and Richardson, ibid., 62, 130 (1940).

(5) The RCl was added in ten minutes at 17°. The solution was cooled to 0° after five hours and treated with 44.87 cc. of 1.334 N iodine in benzene. The mixture was filtered by suction, the residue washed with benzene, and the filtrate titrated with 0.874 N thiosulfate. The yield was 34.7% of theoretical.

(6) In this experiment the iodine was added rapidly. The yield of amylsodium was estimated to be 36.3%.

(7) Experiment (4) was repeated, but the product was treated with 85 cc. of 1.048 N iodine at 0° for five minutes, then filtered and washed with benzene. The filtrate was titrated with 0.833 N thiosulfate. The yield was found to be 52.4% of the theoretical, compared to about 45% determined by carbonation.

J. Organomagnesium compounds.

The Grignard reagents were prepared from the alkyl bromides by the ordinary procedure. A dry three-necked flask was swept with nitrogen; magnesium equivalent to the alkyl halide to be used was added, then a portion of the ether, and a small crystal of iodine. A little of the alkyl halide dissolved in ether was added, and the mixture was warmed until the iodine color disappeared. The mixture was then stirred and the remainder of the halide was added slowly.

When long-chained alkyl chlorides were used, the

reaction was started by heating the magnesium with ether, a few drops of n-butyl bromide, and a crystal of iodine. When the iodine color disappeared, the alkyl chloride was added quickly and the mixture was refluxed for twelve to twenty-four hours. Stirring was not required.

The normality was determined by titration with N/10 sulfuric acid, with methyl orange as the indicator. The volume was estimated by comparison with water in a similar flask; this method cannot be expected to give very good results, since the surface of the liquid is very large relative to the volume. The values obtained for the percentage yield are therefore accurate only to within a few percent. The reason for the high value in experiment (2) is not known; the volume and normality were both checked carefully. An error in weighing out the n-dodecyl chloride is the most probable cause. The results are shown in Table 13.

Table 13

Preparation of Grignard Reagents

No.	Alkyl halide	RX Moles	Ether in cc.	N of RMgX	Yield in %
(1)	n-Dodecyl bromide	0.1	125	0.781	67.1
(2)	n-Dodecyl chloride	0.12	125	0.845	112
(3)	n-Tetradecyl bromide	0.05	90	---	70.8
(4)	" "	0.1	100	0.562	87.2
(5)	" "	0.1	125	0.565	76.3
(6)	" "	0.125	120	0.664	62.6
(7)	" "	0.022	20	0.332	41
(8)	n-Hexadecyl bromide	0.055	55	---	83.5
(9)	" "	0.075	75	0.482	79.7
(10)	" "	0.075	75	0.387	66.5
(11)	" "	0.05	50	---	73.5
(12)	n-Hexadecyl chloride	0.1	125	0.795	95.5
(13)	n-Hexadecyl iodide	0.035	35	0.187	40
(14)	n-Octadecyl bromide	0.044	45	---	86.8

K. Organocalcium compounds.

1. Hexadecylcalcium iodide.-- (1) Fourteen and nine-tenths grams of n-hexadecyl iodide (0.04 mole) was dissolved in 25 cc. of dry ether. Four and eight-tenths grams (0.12 atom) of calcium metal (Dow Chemical Co., order no. 1259, 2-11-41) was cut with scissors and dropped into 50 cc. of ether in a nitrogen-filled three-necked flask. The hexadecyl iodide solution was added in several portions, with stirring and refluxing. Color test number I was negative after fifteen hours. n-Propyl iodide (1 cc.) was added and refluxing was continued. The only evidence of reaction was a small amount of white precipitate.

(2) Four and eight-tenths grams of calcium was filed directly into 25 cc. of ether in a nitrogen-filled three-necked flask. To this were added a small crystal of iodine, and 0.9 g. of iodobenzene (0.0044 mole). The mixture was refluxed for an hour; color test number I was then strongly positive. The ether solution of phenylcalcium iodide was decanted, and the calcium washed twice with ether, then covered with 30 cc. of ether. Color test number I was negative. To this activated calcium was added 14.1 g. (0.04 mole) of n-hexadecyl iodide in 20 cc. of ether, slowly. Reaction started at once; there was spontaneous refluxing, and a voluminous white precipitate formed. The mixture was allowed to stand overnight, then was warmed (since at room temperature it was nearly solid), stirred and refluxed. It was filtered through asbestos under nitrogen. The yellowish filtrate gave a green color in color test number I (positive), and 5 cc. required 2.75 cc. of 0.0987 N sulfuric acid for neutralization; this corresponded to a 14.2% yield of RCaI. The residue was washed with 50 cc. of petroleum ether (A), but the filtrate did not give a color test number I or require more than a few drops of acid for neutralization. The washed residue gave a positive color test number I.

The ether filtrate was carbonated with dry ice, dried and distilled. "Hexadecane" distilled at about 140-175° at 26 mm.; n_D^{20} 1.4387; yield 2.1 g. (23.2%). Margaric acid distilled at 195-215° at 26 mm. but was not pure and was not

definitely identified.

(3) The second experiment was repeated. The unfiltered mixture was carbonated with dry ice four hours after the start of the reaction. The product was hydrolyzed, acidified, dried and distilled. The products obtained were:

a. "Hexadecane," 3.2 g. (35.4%), b.p. 183° at 43 mm., n_D^{20} 1.4381. From this it was estimated that the fraction contained 36.2% of hexadecene.

b. Margaric acid, 1.3 g. (12.6%), m.p. 54°, soluble in aqueous potassium hydroxide.

c. Dotriacontane (residue), 3.7 g. (41%).

2. **Attempt to prepare dodecylcalcium bromide.**-- Five grams of filed calcium metal (0.125 atom) was activated with iodine and iodobenzene as in the previous experiments, and the phenylcalcium iodide was washed out with ether. To the activated calcium were added 12.5 g. (0.05 mole) of n-dodecyl bromide and 20 cc. of ether. After one hour of refluxing a color test number I was negative. A small crystal of iodine was added and the mixture was refluxed overnight; color test number I was negative. After a total of forty-six hours of refluxing, color test number I was still negative on both the solution and the solid. Titration of 5 cc. required 0.71 cc. of 0.0987 N sulfuric acid. This would indicate a 1% yield of dodecylcalcium bromide.

L. Miscellaneous compounds.

1. Dodecylpotassium.-- Eight and six-tenths grams
(0.22 atom) of clean potassium metal was heated under xylene
to 75° and shaken. Petroleum ether (B) was added to make the
metal sand sink more quickly; the solvents were decanted and
replaced with petroleum ether (A). The potassium sand was
flushed into a 250 cc. three-necked flask filled with nitro-
gen. About 90 cc. of solvent was used. The flask was cooled
in a bath of petroleum ether and dry ice, to about 0°. Ten
and two-tenths grams (0.05 mole) of n-dodecyl chloride was
added during one hour. A color test number I (filtered
before hydrolysis) was positive forty-five minutes from the
start. Color test number IV (110) was positive. The mixture
was allowed to warm to room temperature. The supernatant
liquid was clear and colorless, and gave a negative color test
number I. The suspension was poured into dry ice after a
total of four hours. It was decomposed with methanol, hy-
drolyzed and acidified. The organic layer was dried and
distilled. There was obtained 4.5 g. (52.9%) of "dodecane",
n_D^{20} 1.4262; the proportion of dodecene in this was estimated
to be 30.5% (this means that the yield of dodecane was 36.8%
of the theoretical, while that of dodecene was 16.1%). In
addition there was 1.1 g. (10.3%) of crude tridecylic acid
and 2.0 g. (23.7%) of tetracosane. The acid melted at 35-41°;
recrystallization by reprecipitation from aqueous KOH altered

this to 39-40°. The melting point of tridecylic acid is reported to be from 40° to 42° (117).

2. Attempts to prepare organocopper compounds.-- (1) Seventy cubic centimeters of 0.115 N octadecyllithium in ether was cooled to -10° in an ice-salt bath. To this was added 1.5 grams of cuprous iodide. The color slowly darkened to a deep brown. A color test number I was negative. The brown solid was washed several times with ether; when dried it burned quietly, but left a residue and gave a green color to the flame. A silver nitrate test showed the presence of a small amount of halogen. Hexatriacontane was isolated, but this probably came from the reaction between octadecyl bromide and lithium.

(2) To 0.03 mole of n-tetradecyllithium in ether, cooled to -10°, was added 5.85 g. (0.015 mole) of cuprous iodide. Within a minute the mixture was black. A color test on the suspension was negative four minutes after the iodide was added. The solid was washed with ether, then with water, and dried. The dry material contained 59.7% and 59.0% of copper by analysis. The theoretical copper content of cuprous iodide is 33.4%. The analyses thus indicated some free copper, which may have come from decomposition of tetradecylcopper. Octacosane was isolated.

3. Attempts to prepare organobarium compounds.-- (1) Two grams of barium metal (Fischer Scientific Company, 99% Ba

metal, fused; lot number 421717; H42)* was filed into 20 cc. of dry ether in a 250 cc. three-necked nitrogen-filled flask. To this were added 5.2 g. of barium cut with scissors, and 0.2 g. of iodine. This was refluxed for one-half hour, then seven grams of n-dodecyl iodide was added and refluxing was continued. A color test number I was negative after two hours. More dodecyl iodide was added, to a total of 14.8 g. (0.05 mole); 30 cc. of ether was added, and refluxing was continued. Color tests on solution and residue were negative after forty-eight hours.

(2) The technique used for preparing dodecyllithium in petroleum ether was used. Six and nine-tenths grams of barium was refluxed with 50 cc. of petroleum ether (B) and a small crystal of iodine for fifteen minutes. To this was added 10.2 grams (0.05 mole) of n-dodecyl chloride. Refluxing was continued for fifty hours. A color test number I was negative both on the solution and on the solid. There was a small amount of white precipitate.

(3) Twelve and one-half grams of n-dodecyl bromide (0.05 mole) and 6.9 g. of barium (0.05 atom) were heated nearly to boiling. The only sign of reaction was a small amount of white precipitate. Twenty-five cubic centimeters of dry ether and a crystal of iodine were added to the cooled mixture. The mixture was refluxed under nitrogen. After nine days a

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* Analysis showed 97.7% barium, no calcium, and a trace of strontium.

color test number I was still negative.

(4) Five and one-half grams of n-tetradecyl iodide was warmed with 2.5 g. of barium and a trace of iodine. The iodine color disappeared quickly; then the mixture darkened and became turbid. Color test number I was negative on the suspension. Mercury (1.9 g.) was added and the mixture was again heated nearly to refluxing. After five days the color test was still negative.

4. Attempts to prepare organoaluminum compounds. -- Two and six-tenths grams of aluminum chloride (0.0195 mole) in 28 cc. of dry ether was added to the Grignard reagent prepared from 15 g. (0.06 mole) of n-dodecyl bromide. Gentle refluxing occurred, and a white precipitate formed. Some of the solution was removed and dried in air. It was not spontaneously inflammable. The solution gave a precipitate with ammonia. A color test number I was negative, even when heated. The ether was removed in a current of nitrogen, the residue was extracted with 50 cc. of petroleum ether (B), and the solution was filtered through asbestos under nitrogen. Analysis of the filtrate gave the following values, expressed as molarities:

Aluminum	0.153 M
Magnesium	0.031 M
Chloride	0.018 M
Bromide	0.021 M

Color tests were run for several days but were all negative.

The Grignard reagent prepared from 15 g. of dodecyl bromide (0.06 mole) was treated with 2.6 g. of aluminum chloride in ether. The ether was distilled off in a stream of nitrogen, and replaced with 130 cc. of petroleum ether (A). The solution was filtered under nitrogen and the filtrate was concentrated to about 50 cc., then cooled in ice. The white precipitate which formed was filtered off and recrystallized from petroleum ether (A). The solid was dried in a stream of nitrogen. The yield was 7.28 g. of aluminum compound.

<u>Anal</u>. Calc'd for $C_{36}H_{75}Al$: Al, 5.05%. Found: Al, 4.63%; Cl, 1.58%.

5. <u>Attempt to prepare tridodecylantimony</u>.-- This was prepared, in a manner similar to that used to make tridodecyl-arsenic, from the Grignard reagent and antimony trichloride. The ether was removed in a stream of nitrogen. An attempt was made to distill the residue; but decomposition occurred when the bath reached 260°. No further attempts were made to prepare this compound.

M. <u>Determination of mixed melting points</u>.

Approximately equal quantities of various pairs of mercury, lead, and tin compounds were mixed and the melting points were determined. The results are shown in Table 14.

Table 14

Mixed Melting Points

A	m.p. - $^{\circ}C$	B	m.p. - $^{\circ}C$	A - B m.p. -$^{\circ}C$
$C_{12}H_{25}HgBr$	108-108.7	$C_{14}H_{29}HgBr$	110-110.5	102-103
$C_{16}H_{33}HgBr$	110.5-111.5	$C_{18}H_{37}HgBr$	110-111	107-109
$(C_{16}H_{33})_2Hg$	61-62	$(C_{18}H_{37})_2Hg$	66.5-67	60-67
$C_{16}H_{33}HgCl$	114-115	$C_{18}H_{37}HgCl$	115-116	113
$C_{16}H_{33}HgCl$	114-115	$C_{12}H_{25}HgCl$	114-114.5	108-109
$C_{18}H_{37}HgCl$	115-116	$C_{18}H_{37}HgBr$	110-111	109-110
$C_{12}H_{25}HgI$	91	$C_{16}H_{33}HgI$	93-93.5	83-84
$C_{16}H_{33}HgBr$	110.5-111.5	$C_{16}H_{33}HgI$	93-93.5	92-95
$(C_{12}H_{25})_3PbCl$	64-65	$(C_{14}H_{29})_3PbCl$	74-75	66-67
$(C_{16}H_{33})_4Pb$	42	$(C_{16}H_{33})_4Sn$	41.5-42.5	42
$(C_{16}H_{33})_3SnCl$	55.5-56.5	$(C_{18}H_{37})_3SnCl$	61-62	56-57
$(C_{16}H_{33})_4Sn$	41.5-42.5	$(C_{16}H_{33})_3SnCl$	55.5-56.5	52-55
$(C_{16}H_{33})_4Sn$	41.5-42.5	$(C_{18}H_{37})_4Sn$	47	42-47

N. Methods of analysis.

1. Mercury.-- Mercury was determined by modifications of the method of Tabern and Shellberg (97).

(1) Mercury in the absence of iodine.-- The sample containing about 0.1 g. of mercury, was weighed into a 125 cc. round-bottomed flask connected by a ground glass joint to a reflux condenser. Ten cubic centimeters of fuming sulfuric acid were added, and the mixture was warmed until the mercurial had become dispersed in the acid. To this was added,

in small portions, 30% hydrogen peroxide, until the solution
became straw-colored or colorless. The solution was then
heated to decompose the excess hydrogen peroxide; very often
it darkened during this treatment and more peroxide had to be
added to bleach it again. After the peroxide had been decom-
posed, the solution was cooled somewhat, and diluted with
water to about 50 cc. It was then filtered. In some cases a
small amount of white solid, presumably paraffinic, remained
after decomposition, but this did not affect the results. The
filtrate was saturated with hydrogen sulfide; the mercuric
sulfide was filtered through a Gooch crucible and washed care-
fully with water, alcohol, carbon disulfide, and ether, then
dried in the oven at about 140°.

(2) Mercury in the presence of iodine.-- The sample was
decomposed as before. The iodine in the condenser was washed
into the flask with water, and the solution was diluted to
about 60 cc. Aluminum metal was added in four portions of
0.2 g. each, with warming after each addition. The precipi-
tate was reddish at first, but finally became greenish. The
mixture was filtered with suction through a small filter paper
(too much paper interferes in the following step). The amalgam
and the green precipitate were returned to the flask and heated
under reflux with 4 cc. of concentrated nitric acid, followed
by 10 cc. of bromine water. The paper was filtered out, and
dilute sodium bisulfite solution was added drop by drop until
the color disappeared permanently. The mercury was precipitated

as the sulfide, as before.

(3) Mercury in the presence of arsenic.-- The sample was
decomposed with fuming sulfuric acid and 30% hydrogen peroxide.
The mercury and arsenic were precipitated as the sulfides,
filtered, and washed first with water, and then with ammonium
chloride solution. The Gooch crucible was then filled with
concentrated ammonium hydroxide, which was allowed to drain
slowly. The treatments with ammonium chloride and ammonia
were repeated. The residual sulfide was washed with water,
alcohol, carbon disulfide, and ether, and dried at 140° (102).

2. Arsenic.-- The method of Tabern and Shellberg (97) was
followed. The decomposition of the long-chained trialkyl ar-
sines was very difficult. Enough sample to contain about
0.1 g. of arsenic (0.9 g. in the case of tridodecylarsenic)
was weighed into the flask used for mercury analyses, and
warmed with 12 cc. of fuming sulfuric acid. Hydrogen peroxide
(30%) was added until most of the brown material had disappeared;
this required ten to fifteen minutes. Then the sample was re-
fluxed with occasional addition of hydrogen peroxide for four
or five hours to remove the last portion of undecomposed
material. The solution was transferred to a beaker and di-
luted to about 125 cc., then treated with 10 cc. of potassium
iodide (10%) and boiled to remove the iodine liberated. When
the solution was concentrated below 50 cc. a reddish precipi-
tate began to form, and spattering occurred. The solution
was then diluted slightly to dissolve this precipitate, and

a little NaHSO$_3$ was added to destroy the last trace of iodine.
It was boiled to remove any SO$_2$, diluted, and cooled. It was
made slightly alkaline to litmus with 30% sodium hydroxide,
then slightly acid with dilute sulfuric acid. Ten grams of
sodium bicarbonate were added, the mixture was cooled, and
titrated with N/10 iodine in potassium iodide.

3. Lead.-- The method of Gilman and Robinson (106) gave
excellent results.

4. Tin.-- The method of Gilman and King (108) was used,
with the omission of the treatment with bromine solution.
Several additions of nitric acid were required; hydrogen per-
oxide aided in the decomposition.

5. Double titration method for organolithium solutions.--
This method was devised by Haubein (4) to determine the amount
of organolithium compound in a solution containing other basic
substances. Two aliquots were removed; one was added to water
and titrated with N/10 sulfuric acid using methyl orange as
the indicator. The other aliquot was added to about 1 cc. of
benzyl chloride in 10 cc. of anhydrous ether, then hydrolyzed
and titrated with N/10 sulfuric acid. The first titration
(3) gave the total base present, the second gave the lithium
not attached to carbon. The difference represented the
amount of the organolithium compound.

O. The preparation of long-chained halides.

1. Alkyl chlorides.-- The long-chained alcohols were
dissolved in benzene and warmed with an excess of thionyl
chloride in the presence of a small amount of pyridine (121,
122). The yields were about 83-88% of the theoretical. It
was found essential to use purified thionyl chloride; the
"practical" grade gave very poor results in several cases.
Most of the dodecyl chloride used was purchased from the
Eastman Kodak Company.

2. Alkyl bromides.-- The alcohols were refluxed with 48%
hydrobromic acid and concentrated sulfuric acid, the products
were separated, then treated with concentrated sulfuric acid.
The acid was carefully drawn off, and the bromide was diluted
with petroleum ether and washed with aqueous-alcoholic ammonia,
then with water, then dried and distilled (123, 124). This
method always gave considerable trouble, because of the emul-
sions which formed in the extraction of the alkyl sulfates
from the bromides. A preliminary distillation of the crude
bromides decreased this difficulty (125). The yields were

121. M. R. McCorkle, Ph. D. Thesis, Iowa State College (1938)
     p. 70.

122. Clark and Streight, Trans. Roy. Soc. Canada, (3) 23,
     Sect. 3, 77 (1929).

123. Kamm and Marvel, Org. Syntheses, Coll. Vol. 1, 27 (1932).

124. Reid, Ruhoff, and Burnett, Org. Syntheses, 15, 24 (1935).

125. Urquhart, Gates, and Connor, ibid., 21, 36 (1941).

about 60-70%. Dodecyl, tetradecyl, and hexadecyl bromides were also purchased from the Eastman Kodak Company.

3. Alkyl iodides.-- The method of Levene and West (126), using phosphorus and iodine with the alcohol at 170°, gave good results. The yields were about 90-95%.

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126. Levene and West, J. Biol. Chem., 18, 477 (1914).

IV. DISCUSSION

Moore (127) and Gilman, Langham and Moore (23) have pointed out several advantages of using low-boiling petroleum ether as the solvent in the preparation of organolithium compounds. Moore (127) stated that (a) the rate of formation approached that in ether, and higher yields were obtained; (b) the difficulty of secondary reactions like cleavage, present in diethyl ether, was obviated; (c) indirect supplementary analyses (5) were unnecessary to determine the titer of the solution, and the simple acid-titration method was adequate; (d) the by-product of the reaction, lithium halide, as well as other inorganic compounds such as the oxide and nitride, were insoluble in petroleum ether and were removed by filtration (23). Gilman, Langham, and Moore (23) found that higher-boiling fractions of petroleum ether appear to be less satisfactory; no experimental results were given to show how much less satisfactory.

In the preparation of long-chained lithium compounds, low-boiling petroleum ether has not been found to be as satisfactory as in the case of the lower homologs. The rate of formation was very much slower than in ethyl ether, and the yields were lower. Indirect supplementary analyses were

127. F. W. Moore, Ph. D. Thesis, Iowa State College (1941), p. 33.

found to be necessary (4); although it is true that the difference between the single titration (3) and the double titration (4) values was smaller in petroleum ether than in ethyl ether, nevertheless, it amounted to 15 or 20 per cent of the total. From this it must be concluded either that some basic inorganic lithium compounds are soluble, or may be colloidally dispersed, in petroleum ether, or that the benzyl chloride double titration method (4) does not give a true measure of the amount of organolithium compound dissolved. Higher-boiling fractions of petroleum ether gave better results with the long-chained compounds than did the low-boiling solvent. The reaction was slow at room temperature, but at reflux temperature it proceeded about as rapidly as it did in ethyl ether. The yields were almost as good as those in ethyl ether. As a matter of fact, to measure the yield of an alkyllithium compound in ethyl ether, one must filter and titrate the solution quickly, for the double-titration yield decreases with time at a very appreciable rate /(4) and Table 2, note (b), in this thesis/.

In benzene the preparation of long-chained lithium compounds proceeded in much the same way as it did in petroleum ether (60-68°); the procedure was about the same, the reaction went at approximately the same speed, and the yields were of the same order. Chlorides were again much more suitable than bromides.

Toluene was much less satisfactory than benzene as a

solvent for the preparation of dodecyllithium. The solution
of dodecyllithium in toluene gradually became yellow, and it
was thought that this might indicate the formation of benzyl-
lithium, but careful examination of the products of carbona-
tion failed to disclose any phenylacetic acid. Pacevitz (128)
failed to isolate phenylacetic acid from carbonation of the
products of reaction of n-butyl chloride with lithium in tolu-
ene, but when n-butyl bromide was used a very small yield of
phenylacetic acid was obtained. n-Butyllithium in ether also
metalated toluene laterally, but ethyllithium did not metalate
it at all. The lithium compounds are considerably less re-
active than organosodium compounds in this respect.

In ethyl ether the long-chained chlorides or bromides
reacted with about equal rapidity with lithium, and showed no
less reactivity than did the butyl halides and other short-
chained homologs. The long-chained chlorides used showed a
marked advantage over the bromides; whether this was entirely
due to actual superiority of the chlorides per se, or par-
tially to the impurities in the bromides, is not known. In
comparing the yields of long-chained lithium compounds with
the already published yields of short-chained lithium com-
pounds (1, 127), the single titration values given in this

128. H. A. Pacevitz, Ph. D. Thesis, Iowa State College (1940),
     p. 108.

129. Gilman, Willis, Cook, Webb, and Meals, J. Am. Chem. Soc.,
     62, 667 (1940).

thesis should be used rather than the double titration values.
When this is done, the yields for long-chained compounds are
seen to be as good as those for the shorter-chained homologs,
in ethyl ether. In benzene and petroleum ether the shorter
homologs have given better results, but it is possible that
further work will show this to be incorrect.

One metalation was carried out with n-dodecyllithium.
Pyrogallol trimethyl ether and dodecyllithium yielded, on car-
bonation, 2,3,4-trimethoxybenzoic acid. While this experiment
has not been duplicated with butyllithium, the result conforms
to the rule that organolithium compounds metalate ortho to
the ether linkage (127). Dodecyllithium was found not to
metalate benzene.

Long-chained bromides have been used in these laboratories
for the preparation of lithium compounds (6, 7). The chlorides
are preferable for three reasons: (a) gram for gram, as well
as mole for mole, the chlorides are cheaper, and are easier
to prepare than the bromides; (b) the chlorides do not appear
to deteriorate in storage, while the bromides apparently do;
(c) the chlorides almost invariably give better yields than
do the bromides, in any solvent.

The use of unsaturate-free petroleum ether for the prepa-
ration of alkyllithium compounds is not necessary. Morton,
Fallwell, and Palmer (130) found that there was very little

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130. Morton, Fallwell, and Palmer, ibid., 60, 1426 (1938).

advantage in the use of unsaturate-free petroleum ether
($35-60^o$) in the preparation of amylsodium, though in the case
of the higher-boiling petroleum ether ($90-120^o$) an increase
of 20% in the yield was observed when unsaturate-free solvent
was used. Moreover, the products of the reaction include,
e.g., in the case of dodecyllithium, dodecene, so even if the
solution is unsaturate-free at the beginning, it may not be
at the end of the reaction.

Morton and his co-workers (15, 16, 17, 120, 130, 131)
showed that alkylsodium compounds can be prepared directly
from alkyl halides and metallic sodium. They estimated the
amounts of organosodium compounds present by passing in carbon
dioxide gas. The products isolated were, in the case of
n-amyl chloride, caproic acid and butylmalonic acid. The
latter was believed to have come from amylidenedisodium.

Pacevitz (128), Gilman and Pacevitz (132), and Gilman,
Pacevitz and Baine (133) differed from Morton in two ways.
The yields of amylsodium prepared by them from the amyl chlo-
ride and sodium were not as high as those reported by Morton,
and the ratio of caproic acid to butylmalonic acid was dis-
covered to be dependent on the rate of carbonation. The most
probable explanation of the first point is that one of the

131. Morton, Richardson, and Hallowell, ibid., 63, 327 (1941);
this is the latest of a series of twenty papers on con-
densations by sodium.

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

133. Gilman, Pacevitz, and Baine, ibid., 62, 1514 (1940).

principal factors determining the yield of amylsodium is the
amount of sodium used (16); further, this seems to be a
function of the area of sodium exposed, rather than of the
weight of sodium (134). There does appear in the work de-
scribed in this thesis to be a dependence of the ratio of
normal acid to alkylmalonic acid on the rate of carbonation,
but the ratio was found to be more nearly the same as that
reported by Morton and Richardson (120) than Pacevitz (128)
found, even when rapid carbonation was used. The method of
separation of the acids described by Morton (15) was em-
ployed. For experiments that corresponded as nearly as pos-
sible except in respect to fineness of sodium and rate of
carbonation, the recovery of caproic acid was 27% and of
butyl malonic acid was 14%; Morton and Richardson (120) ob-
tained 68% and 21%, respectively. Pacevitz (128) isolated
only very small amounts of butylmalonic acid from rapidly
carbonated amylsodium.

The formation of dodecane and dodecene from dodecyl
chloride and sodium was expected, for the Wurtz reaction has
long been known to give these so-called "disproportionation"
products as well as the coupling product (12). Morton and
Fallwell (135) isolated pentane and pentene from amylsodium
reactions.

It was shown here that dodecane always occurs in

134. Morton and Hechenbleikner, ibid., 58, 2599 (1936).
135. Morton and Fallwell, ibid., 59, 2387 (1937).

somewhat greater quantity than dodecene; similarly in the
case of hexadecylsodium, hexadecane forms in excess of hexa-
decene. This is explained according to Morton's theory by
the assumption that two dodecyl radicals disproportionate to
form either a mole of dodecane and a mole of dodecene, or else
to form a mole of dodecane and a free dodecylidene radical.
According to Pacevitz (128) the excess of dodecane would be
formed when dodecylsodium metalated sodium tridecylate. No
appreciable amounts of undecylmalonic (or pentadecylmalonic)
acids were obtained, however, and the ratio of the dodecane
to the dodecene was the same before carbonation as it was
after (Table 11, number 8). It was thought that the extra
hydrogen might come from the solvent, petroleum ether, but
measurement of the unsaturation of the solvent before and after
use in the preparation of dodecylsodium failed to show any
increase in unsaturation (Table 11, number 11). The work re-
ported is not consistent in this respect. Either the long-
chained alkylmalonic acids are more soluble in petroleum
ether than has been reported (136), or the analysis of the hydro-
carbon is at fault /though the method has been found to be
reliable (137)7, or the extra hydrogen came from traces of
water. The usual precautions were taken to eliminate the
latter possibility.

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136. Hell and Sadomsky, Ber., 24, 2778 (1891).

137. Faragher, Gruse, and Garner, Ind. Eng. Chem., 13, 1044
(1921).

The heterogeneity of the alkylsodium mixtures eliminates the analysis by aliquots; so each run has to be analyzed as a whole. Since the yields vary somewhat even when the conditions are controlled closely, it is difficult to evaluate the various methods of analysis. Carbonation is the accepted standard method, and reaction should be complete since carbon dioxide is reasonably soluble in the solvents used (138), and there are few side reactions. Iodination gave higher results than carbonation consistently; it should give lower results if the secondary reaction
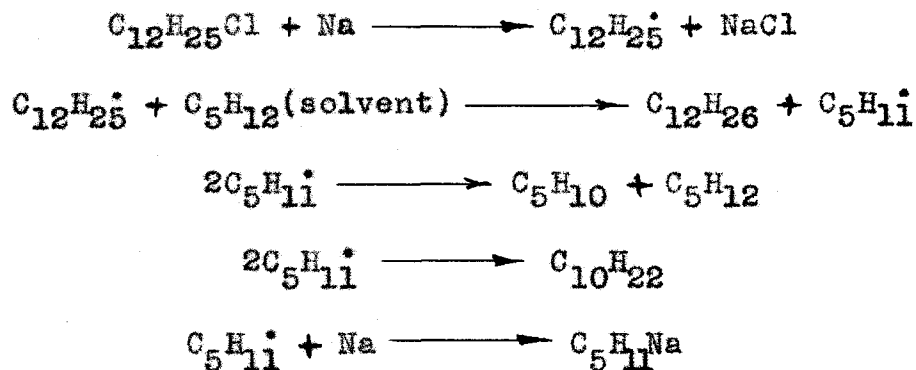
$$RNa + RI \longrightarrow RR + NaI$$

were the only side reaction. Iodine does not react very rapidly with sodium metal, although it does react. It does not add readily to dodecene. It reacts rapidly with aqueous alkali, but care was taken to remove alkaline materials before hydrolysis, in the iodimetric analysis. The cause for the high results obtained by iodimetric titration of sodium compounds is therefore not known. With Grignard reagents the method has been reported to give low results (3).

The cleavage of ether by dodecylsodium does not proceed so rapidly that the sodium compound cannot be made in this solvent (Table 11, number 10). The high ratio of dodecane to dodecene obtained in this case, and the unusually high proportion of the disproportionation products are to be particularly noted.

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138. Just, Z. physik. Chem., 37, 342 (1901).

Hey and Waters (139) stated that the free alkyl radicals are very reactive and can have only a transient existence. They react with the first molecules they encounter, which are usually the solvent molecules. Hey and Waters also claimed that no solvent has yet been discovered which is inert to free neutral radicals, and that in this way the latter may be differentiated from free ions, which are often stable in solution. It is hard to reconcile this view with that of Morton, that free radicals are the intermediates in the formation of organosodium compounds. If free radicals were the intermediates, and were as reactive as Hey and Waters concluded, then we would expect a chain of reactions to be set up, such as:

$$C_{12}H_{25}Cl + Na \longrightarrow C_{12}H_{25}^{\cdot} + NaCl$$

$$C_{12}H_{25}^{\cdot} + C_5H_{12}(solvent) \longrightarrow C_{12}H_{26} + C_5H_{11}^{\cdot}$$

$$2C_5H_{11}^{\cdot} \longrightarrow C_5H_{10} + C_5H_{12}$$

$$2C_5H_{11}^{\cdot} \longrightarrow C_{10}H_{22}$$

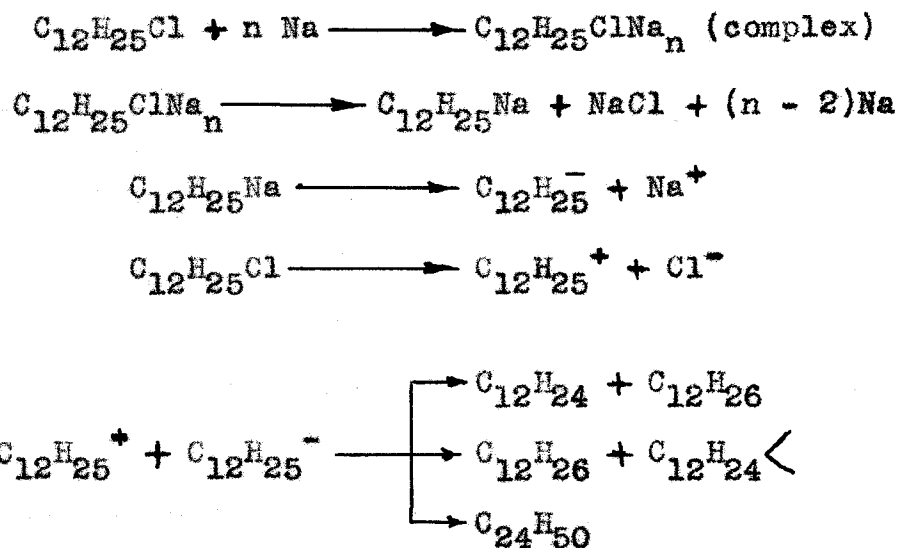$$C_5H_{11}^{\cdot} + Na \longrightarrow C_5H_{11}Na$$

There was no evidence that such reactions occurred, even to a minor extent. The products formed in the reactions of alkyl chlorides with sodium, followed by carbonation, can be explained without the assumption of free radicals, and in view of the difficulty pointed out, this seems advisable.

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139. Hey and Waters, Chem. Rev., 21, 169 (1937).

Free ions, or complex formation, offer more plausible explanations; perhaps both may be involved. The same objection as that just discussed may be raised to Späth's (22) free radical theory in the reaction of methylmagnesium iodide with hexadecyl iodide in ether.

A free ion theory of the Wurtz reaction would eliminate the difficulty. According to it, the Na -- C and Cl -- C bonds are both ionic, or sufficiently polarizable to split ionically:

$$C_{12}H_{25}Cl + n\ Na \longrightarrow C_{12}H_{25}ClNa_n \text{ (complex)}$$

$$C_{12}H_{25}ClNa_n \longrightarrow C_{12}H_{25}Na + NaCl + (n-2)Na$$

$$C_{12}H_{25}Na \longrightarrow C_{12}H_{25}^- + Na^+$$

$$C_{12}H_{25}Cl \longrightarrow C_{12}H_{25}^+ + Cl^-$$

$$C_{12}H_{25}^+ + C_{12}H_{25}^- \longrightarrow \begin{cases} C_{12}H_{24} + C_{12}H_{26} \\ C_{12}H_{26} + C_{12}H_{24} < \\ C_{24}H_{50} \end{cases}$$

The last equation would account for the formation of the amylidene "radical," which, since it is not an "odd molecule," might not be expected to be as reactive as a true free radical. Thus, it might add sodium, but not extract hydrogen from the solvent molecule.

Morton and his co-workers found that the yields of organosodium compounds from alkyl halides and sodium were --

(a) greater at low temperatures (140); (b) greater with chlorides than with bromides or iodides (15); (c) higher in low-boiling petroleum ether than in high-boiling fractions (134); (d) greater, the higher the proportion of sodium to the alkyl halide (16); (e) slightly higher at lower concentration (134). These things have been found to hold true for dodecylsodium and hexadecylsodium also. The most important factors were the nature of the halide (b), the solvent (c), and the ratio of sodium to halide (d); temperature, time, and amount of solvent were minor factors, within reasonable limits.

Potassium metal behaved with dodecyl chloride very much like sodium, but the yield of dodecylpotassium was lower than that of dodecylsodium under similar conditions.

The observations of Schlenk and Holtz (13) on the insolubility of organosodium compounds were confirmed. Hexadecylsodium was observed to be insoluble in petroleum ether (b.p. 30-35°), while n-dodecylsodium was insoluble in kerosene (Table 11); the kerosene distilled within the boiling ranges of dodecane and tetradecane; so it may be said that n-dodecylsodium is insoluble in dodecane. n-Dodecylpotassium was equally insoluble in petroleum ether (b.p. 30-35°).

The data obtained on the yields of Grignard reagents are offered merely to show the results that are obtained, using commercial halides, or halides prepared with ordinary care.

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

The percentage yields are in general lower in small preparations, lower with iodides than with bromides, and lower with bromides than with chlorides. The careful experiments of Houben, Boedler, and Fischer (27) indicated much less difference between bromides and iodides than the single preparation with an iodide indicated here (Table 13).

Hexadecyl iodide and calcium gave about as good yields of organocalcium compound as are obtained with the shorter chains such as ethyl or butyl (4). It is interesting to note that here, as in the case of the reactions with sodium and potassium, the disproportionation products were obtained in high yield, and the proportion of olefin to paraffin was about 1 to 1.75. Hexadecylcalcium iodide was soluble in ether, did not cleave ether rapidly, if at all, and could be titrated by the ordinary procedure (3). With respect to ether cleavage, hexadecylcalcium iodide was less reactive than dodecyllithium. Since increasing chain length increases rather than decreases the activity of lithium alkyls toward ether (4) it is probable that hexadecyllithium cleaves ether more rapidly than hexadecylcalcium iodide. Dodecyl bromide did not react with calcium.

The four attempts to make long-chained barium compounds were unsuccessful. Schulze (141) found that methyl, ethyl, n-butyl, and phenyl iodides did not react with barium metal.

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141. F. Schulze, Ph. D. Thesis, Iowa State College (1927), p. 84.

Grüttner (142) found some evidence for the formation of ethylbarium iodide from ethyl iodide and barium amalgam, but it appears that organobarium compounds are at best very difficult to prepare.

The melting points of the dialkylmercury compounds prepared showed a regular gradation with chain length. The relationship may be expressed as

$$M = 32 + 13 \sqrt{n - 11} \qquad (11 < n < 19)$$

where M is the melting point (Centigrade) and n is the number of carbon atoms in the alkyl group. The dialkylmercurials were very soluble in petroleum ether and in ether, but very slightly soluble in alcohol.

The melting points of the long-chained alkylmercuric bromides did not show sufficient variation with chain length to make these compounds particularly valuable as derivatives of the alkyl bromides (25). The same was true of the chlorides and iodides. The dialkylmercury derivatives were too difficult to purify to be useful as derivatives.

The relationship of the melting point of the alkylmercuric salts to the length of the alkyl chain is rather interesting. If, in order to eliminate the effect of alternation (46), we consider only the chains with even numbers of carbon atoms, it can be seen (Table 15) that the melting

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142. Grüttner, Inaug. Diss. Berlin (1914), p. 84. /Krause and v.Grosse, "Die Chemie der metall-organischen Verbindungen, Borntraeger, Berlin (1937), p. 123.7

points for each group of halides are lowest for the dodecyl-
mercuric salt.

Table 15

Melting Points of Alkylmercuric Halides.

R	RHgCl	RHgBr	RHgI
Ethyl	192° (26)	198° (26)	186° (26)
n-Butyl	130 (26)	129.23030(46)	117 (26)
n-Hexyl	125 (26)	122.0-122.2 (46)	110 (26)
n-Octyl	115-115.5 (143)	114.8-115.0 (46)	---
n-Decyl	---	111.0-111.4 (46)	---
n-Dodecyl	114-114.5	108-108.7	91
n-Tetradecyl	---	110-110.5	---
n-Hexadecyl	114-115	110.5-111.5	93
n-Octadecyl	115-116	110-111	---

The tetraalkyltin compounds showed a regular dependence
of melting point on chain length. It is probable that the
tetradodecyltin, which was difficult to purify, melted some-
what lower than the perfectly pure compound would have. The
melting points of the trialkyltin chlorides were higher as
the length of the alkyl chain increased. Probably here, too,
a minimum melting point is reached somewhere between triethyl-
tin chloride (m.p. 15.5°) and tridodecyltin chloride (m.p.
33°), but no data are available.

The tetraalkyl derivatives of lead prepared resembled the
tetraalkyltin compounds in melting points and solubilities.

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143. Whitmore and Bernstein, J. Am. Chem. Soc., 60, 2626
(1938).

A mixture of tetrahexadecyltin and tetrahexadecyllead showed
no depression in melting point (Table 14). The melting points
of the trialkyllead chlorides were twenty or thirty degrees
higher than the corresponding trialkyltin chlorides in the
range observed. It is obvious that between tri-$\underline{n}$-butyllead
chloride (m.p. 109-111°) and tri-$\underline{n}$-dodecyllead chloride
(m.p. 64-65°) there must occur a minimum in the melting point
(Table 3).

Since the trialkyltin and trialkyllead chlorides show
much greater differences in melting point between homologs
than do the alkylmercuric chlorides, it was hoped that these,
especially the higher-melting lead compounds, might be useful
as derivatives of the long-chained alkyl halides (Tables 2, 3,
and 4). But while mixtures of alkylmercuric halides do show
some melting point depressions, mixtures of trialkyllead or
trialkyltin chlorides do not (Table 14). Unfortunately,
therefore, none of these three series is ideally suited for
derivatization of the long-chained alkyl halides.

The long-chained mercury, tin, and lead alkyls were all
very soluble in petroleum ether. They were not readily solu-
ble in hot alcohol, but were soluble in ethyl acetate, from
which they could be crystallized with or without the addition
of alcohol.

The long-chained alkylmercuric and trialkyltin and tri-
alkyllead chlorides were soluble in hot petroleum ether, ethyl
ether, or ethyl acetate, from which they crystallized on

cooling. Ethyl alcohol had very little solvent action. None of the salts prepared was soluble in water, although tri-dodecyllead nitrate was soluble in alcohol containing a fairly high proportion of water.

V. SUMMARY

A review of the preparation and properties of long-chained organometallic compounds has been made.

A study of the preparation of long-chained alkyllithium compounds in various solvents has been carried out. The advantages of using alkyl halides rather than bromides have been pointed out. Several differences between long-chained and short-chained compounds were observed. The double titration method of analysis has been applied to solutions of long-chained lithium alkyls.

Long-chained alkylsodium compounds were prepared from the alkyl chlorides and sodium metal. The factors influencing the yields were studied. The sodium compounds were not soluble in petroleum ether or in kerosene. Large quantities of dodecane and dodecene were found among the products of reaction between dodecyl chloride and sodium metal.

Several series of long-chained mercury, lead, and tin compounds were made. None was found to be particularly suited for the derivatization of alkyl halides. The relationship between melting point and chain length in several series of salts was studied, and the existence of a minimum point in each group was pointed out.