SOME LONG-CHAINED ORGANOMETAILLIC COMPOLINDS.

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In connection with studies on long-chained types, an examination has been made of some organometallic compounds.

Sodium, Potassium, and Calcium. The RNa, RK and RCaI types examined are insoluble in hydrocarbons including the kerosene fractions. Incidental to the preparation of these RM compounds, there are formed R(-H), RH, and $R \cdot R$ hydrocarbons as a consequence of disproportionation and coupling reactions. The preparation of *n*-dodecylsodium in low yields in ether is of interest because of the ready cleavage of ether by simpler alkylsodium compounds.

Lithium. The RLi compounds (where $R = C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, and $C_{18}H_{37}$) can be prepared in several solvents, but the one of choice appears to be petroleum ether (b.p. 60–70°). The RCl compounds are most suitable for the preparation of the RLi types. 1,2,3-Trimethoxybenzene is metalated by *n*-do-decyllithium in an *ortho*-position, to give subsequent to carbonation 2,3,4-trimethoxybenzoic acid.

Mercury. The long-chained organomercury halides are not particularly suitable as derivatives for rigid differentiation of contiguous even-membered types. For example, $C_{18}H_{33}$ HgCl melts at 114–115°, $C_{18}H_{37}$ HgCl melts at 115–116°, and a mixture of equal parts of these RHgCl compounds melts at 113°. The Experimental Part contains a discussion of some regularities in melting points, and also a broad tabular comparison of mixed melting points.

Tin and Lead. The trialkytin chlorides and the trialkyllead chlorides show greater differences in melting point between homologs than do the alkylmercury chlorides. However, they are only of limited applicability as derivatives for differentiation of contiguous even-membered homologs because of the small melting point depressions of mixtures (see Table IV). It is interesting to note that $(C_{16}H_{33})_4$ Sn melts at 41.5-42.5°, $(C_{16}H_{33})_4$ Pb melts at 42°, and a mixture of equal parts of these R₄M compounds melts at 42°. Two R₄M compounds of high molecular weight were prepared: $(C_{16}H_{33})_4$ Pb, 1107; and $(C_{18}H_{37})_4$ Sn, 1130.

Arsenic. Tri-n-dodecylarsenic distils at 200°/0.009 mm., but tri-n-tetradecylarsenic underwent marked decomposition on an attempted distillation.

EXPERIMENTAL

Organosodium compounds. The procedures for the preparation of the long-chained organosodium compounds were essentially those described by Morton and co-workers (1). *n*-Dodecyl chloride and *n*-hexadecyl chloride were used with powdered sodium. Reaction generally started within 15 minutes; the length of the induction period depended largely

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on the temperature. The start of the reaction was marked by the darkening of the sodium, and the mixture subsequently turned brown and became a sludge. In most cases the mixture was carbonated by pouring directly into a mixture of solid carbon dioxide and ether or petroleum ether. In a few cases carbonation was effected by passing in dry gaseous carbon dioxide. Rapid carbonation converted dodecylsodium to tridecylic acid; slow carbonation gave a mixture of tridecylic acid and undecylmalonic acid. An explanation for the formation of malonic acids in slow carbonations was suggested recently (2).

In one of a number of experiments carried out with *n*-dodecyl chloride (0.0576 mole) and sodium (0.252 g. atom) in petroleum ether (b.p. 28-38°) at 14-25°, the yield of acids was 20.3%; the yield of dodecane was 27%; of dodecene, 25%; and of tetracosane, 19.5%. A similar experiment in ether at 0° gave 0.9% of acids; 71.5% of a mixture of dodecane and dodecene (20%); and 10.3% of tetracosane.

n-Dodecylpotassium. Clean potassium metal (8.6 g. or 0.22 g. atom) was powdered by heating under xylene to 75° and shaking. Petroleum ether (b.p. 60–70°) was added to make the metal sand sink more quickly; the solvents were decanted and replaced by petroleum ether (b.p. 28–38°).

The potassium sand was flushed into a 250-cc. three-necked flask filled with nitrogen. About 90 cc. of solvent was used. The flask was cooled in a bath of petroleum ether and dry ice to about 0°. Then 2.2 g. (0.05 mole) of *n*-dodecyl chloride was added during one hour. A color test I (3) was positive 45 minutes from the start. Color test IV (4) was also positive. The mixture was allowed to warm to room temperature. The supernatant liquid was clear and colorless, and gave a negative color test I. The suspension was poured into dry ice after a total of four hours. The mixture was decomposed with methanol, hydrolyzed, and acidified. The organic layer was dried and distilled to yield: (a) dodecane (36.8%); (b) dodecene (16.1%); (c) tridecylic acid (10.3%); (d) tetracosane (23.7%).

Organolithium compounds. The general procedures were those described in recent publications from this laboratory (5).

Diethyl ether. In general, the RCl compounds were more effective than the RBr compounds, and no examination was made of the RI compounds. The duplicability of results when RBr compounds were used varied somewhat, and freshly distilled RBr compounds are recommended. The yields, by the single acid titration analytical procedure of some comparable experiments are as follows: $n-C_{12}H_{25}Br$ (48%, 65%); $n-C_{12}H_{25}Cl$ (100%); $n-C_{14}H_{29}Br$ (64%); $n-C_{15}H_{33}Cl$ (100%); $n-C_{18}H_{37}Br$ (56%). Carbonation of the RLi compound prepared from $n-C_{16}H_{33}Cl$ gave 51% of margaric acid. In the RLi preparation from $n-C_{12}H_{25}Cl$, the yield calculated by the double-titration procedure of A. H. Haubein (using benzyl chloride) was 76.6%. This yield of 76.6% obtained after one hour, dropped to 41.4% at the end of 53 hours, and to 0% after 143 hours. As has been shown in other studies, the drop in yield is due to ether cleavage.

Petroleum ether $(b.p. 30-35^{\circ})$. The RBr compounds appear to be unsatisfactory for the preparation of RLi compounds in low-boiling petroleum ether. The yields, by the single acid titration of some comparable experiments are as follows: $n-C_{12}H_{25}Cl$ (72%); $n-C_{16}H_{35}Cl$ (63%). In titration in petroleum ether and in benzene, the addition of alcohol hastens the diffusion of lithium from the organic to the aqueous layer and enables the titration to be carried out rapidly. In the $n-C_{12}H_{25}Cl$ experiment, undried, unpurified "Skelly A" (petroleum ether b.p. 28-38°) was used instead of the unsaturate-free solvent, and reaction was started with a little *n*-butyl bromide. After carbonation there was obtained: dodecane (5%); dodecene (4%); tetracosane (28%); and tridecylic acid (36%). Among the products obtained by carbonating the RLi compound from $n-C_{16}H_{35}Cl$ were: a mixture of cetane and cetene (14%); dotriacontane (about 20%); margaric acid (27%); and impure dihexade-cyl ketone (23.5%). The ketone melted at 86-87°, and its oxime at 60°.

Anal. Calc'd for C₃₃H₆₇NO: N, 2.83. Found: N, 3.33.

Petroleum ether (b.p. $60-70^{\circ}$). This petroleum ether appears more satisfactory than the lower-boiling fractions, the yields being better and the time of preparation being signifi-

cantly reduced. The solvent containing the lithium was first boiled, and then the alkyl halide was added during rapid refluxing. No stirring appeared necessary. The reaction was complete in about one hour, during which time the metal gradually sank to the bottom of the flask. The yield of RLi from n-C₁₂H₂₅Cl ranged from 80.3% to 86.2%. With a mixture of equal volumes of pet. ether (b.p. 30–35° and b.p. 60–70°) and a time of 3.5 hours, the yield of n-C₁₂H₂₅Li was 81%; and with a mixture of pet. ether (b.p. 60–70° and b.p. 77–115°) and a time of 1.5 hours, the yield was 77.8%. The pet. ether (b.p. 60–70°) probably can be used effectively with lower RCl compounds, because the yield of n-C₅H₁₁Li from n-C₅H₁₁Cl in one hour was 86.8%.

Aromatic hydrocarbons.—Ziegler and Colonius (6) have shown that benzene is a good medium for the preparation of some RLi compounds. From $n-C_{12}H_{25}Cl$ in benzene and with 15-hour period of reaction, the yield of $n-C_{12}H_{25}Cl$ was 83.4%. Carbonation of this preparation gave a 23% yield of tridecylic acid, and the absence of benzoic acid showed that no metalation took place. There was also isolated, as a product of the carbonation, didodecyl ketone (m.p. 73-74°), the oxime of which melted at 47-48°.

Anal. Cale'd for C₂₅H₅₁NO: N, 3.67. Found: N, 3.58.

The yield of $n-C_{12}H_{25}Li$ from $n-C_{12}H_{25}Cl$ in toluene (one hour) was 28.3%. From $n-C_{12}H_{25}Br$ in benzene (one hour), the yield of $n-C_{12}H_{25}Li$ was 37%.

Metalation of 1,2,3-trimethoxybenzene by n-dodecyllithium. A mixture of 5.4 g. (0.032 mole) of 1,2,3-trimethoxybenzene and 105 cc. of 0.3 N dodecyllithium in pet. ether (b.p. 60-70°) was allowed to stand for 15 hours at room temperature, and then poured into solid carbon dioxide and ether. The 2,3,4-trimethoxybenzoic acid isolated melted at $98-100^{\circ}$. The m.p. reported by Will (7) is 99° .

Anal. Calc'd for C10H12O5: Neut. equiv., 223. Found: Neut. equiv., 228.

n-Hexadecylcalcium iodide. 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. The mixture was refluxed for an hour; color test I was then strongly positive. The ether solution of phenylcalcium iodide was decanted, and the calcium washed twice with ether to remove any phenylcalcium iodide (as **c**hown by a negative color test I).

The calcium, activated by the above procedure, was then covered with 30 cc. of ether, and 14.1 g. (0.04 mole) of *n*-hexadecyl iodide in 20 cc. of ether was added slowly. Reaction set in 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.

The mixture was filtered through asbestos under nitrogen. The filtrate gave a positive color test, and by acid titration analysis gave a yield of 14.2% of RCaI. The residue was washed with 50 cc. of petroleum ether (b.p. $28-38^{\circ}$) and these washings gave no color test, indicating the essential insolubility of RCaI in the petroleum ether. The washed residue did give a color test.

The ether filtrate was carbonated by solid carbon dioxide, and the ether solution was then dried and distilled. The products isolated were: (a) a mixture of hexadecene (12%) and hexadecane (24%); (b) margaric acid (12.6%); and (c) dotriacontane (residue) (41%).

Organomercury compounds. The organomercury halides were prepared from the Grignard reagent and a mercuric halide. In essential accordance with the procedure of Gilman and Brown (8), the mercuric halide was conveniently and automatically dissolved from a Soxhlet thimble into the RMgX solution. Analyses for mercury were by the method of Tabern and Shellberg (9).

Melting points of organomercury compounds. An examination of the melting points in Table II indicates that for each group of RHgX compounds of an even number of carbon atoms, the melting points appear to be at the minimum for the dodecylmercuric salts. It was shown earlier by Vaughn, Spahr, and Nieuwland (10) that there was an alternation of melting point with even and odd members. Some of the trends indicated in Table II

REACTANTS	PRODUCT	M.P. °C	ANAL. $\%~{ m Hg}$	
			Calc'd	Found
$\frac{1}{n - C_{12}H_{25}MgBr + HgBr_2}$	$C_{12}H_{25}HgBr^a$	108-108.7	44.60	45.37
$n - C_{12}H_{28}HgBr + AgOAc$	$C_{12}H_{25}HgOAc^{b}$	64 - 65	46.75	46.5
$(n-C_{12}H_{25})_{2}Hg + HgCl_{2}$	$\mathrm{C_{12}H_{25}HgCl}^{c}$	114 - 114.5	49.5	49.2
$(n-C_{12}H_{25})_{2}Hg + HgI_{2}$	$\mathrm{C}_{12}\mathrm{H}_{25}\mathrm{HgI}^{d}$	91	40.37	40.18
$(n-C_{12}H_{25})_{2}Hg + Hg_{3}(PO_{4})_{2}$	$(C_{12}H_{25}Hg)_3PO_4^e$	84-86	49.97	49.49
$(n-C_{12}H_{25})_{2}Hg + HgSO_{4}$	$(C_{12}H_{25}Hg)_2SO_4f$	160161	47.99	48.10
$n-C_{14}H_{29}MgBr + HgBr_2$	C14H29HgBra	110-110.5	41.98	42.53, 42.69
$n-C_{16}H_{33}MgBr + HgBr_2$	$C_{16}H_{33}HgBr^{h}$	110.5-111.5	39.65	40.42,40.15
$(n-C_{16}H_{33})_2Hg + HgCl_2$	$C_{16}H_{33}HgCl^i$	114-115	43.46	43.25
$(n-C_{16}H_{33})_{2}Hg + HgI_{2}$	$C_{16}H_{33}HgI^{j}$	93-93.5	36.28	35.98
$n-C_{18}H_{37}MgBr + HgBr_2$	$C_{18}H_{37}HgBr^k$	110-111	37.57	37.28
$(n-C_{18}H_{37})_2$ Hg + HgCl ₂	$C_{18}H_{37}HgCl^{\mu}$	115-116	40.97	41.20
$n-C_{18}H_{37}HgCl + NaCN$	C ₁₈ H ₃₇ HgCN ^m	98.5-99	41.80	41.56, 41.46
$n-C_{12}H_{25}MgBr + n-C_{12}H_{25}HgBr$	$(C_{12}H_{25})_{2}Hg^{n}$	44-44.5	37.20	37.44
$n-C_{14}H_{29}MgBr + n-C_{14}H_{29}HgBr$	(C14H29)2Hgo	53-54	33.70	33
$n-C_{16}H_{33}MgBr + n-C_{16}H_{33}HgBr$	$(C_{16}H_{33})_{2}Hg^{p}$	61-62	30.79	30.96
$n-C_{18}H_{37}MgBr + n-C_{18}H_{37}HgBr$	$(C_{18}H_{37})_2Hg^q$	66.5-67	28.35	28.35

TABLE I Organomercury Compounds

^a The crude material melted at 100-110° and weighed 10.87 g. (53.8%). Two crystallizations from ethanol gave the m.p. recorded.

 b The reaction was carried out in 95% ethanol, and the product was crystallized from petroleum ether.

 $^\circ$ Reaction was effected in refluxing 95% ethanol solution, and crytallization was from 95% ethanol.

^d Reaction was effected by refluxing for 15 minutes in dry ether, and crystallization was from petroleum ether.

* Reaction was in absolute ethanol, and recrystallization first from petroleum ether and then from ethanol.

 $^\prime$ Reaction was in a mixture of dry ether and absolute ethanol; and crystallization was from 95% ethanol.

^o The product was crystallized from ethanol. Analyses for bromine by the Parr bomb procedure were low: Calc'd Br, 16.73. Found: Br, 14.3 and 14.3.

^h The first crystallization of the 63.3% yield of RHgBr from petroleum ether (b.p. 60-70°) gave a product melting at 110-111°. Recrystallization from ethyl acetate raised the m.p. to 110.5-111.5°.

ⁱReaction was carried out in ether. Crystallization was first from petroleum ether (b.p. 77-115°) and then from ethyl acetate.

⁷Reaction was carried out by refluxing in ether for 15 minutes. Recrystallization was from petroleum ether (b.p. $60-70^{\circ}$).

^k The product was twice crystallized from petroleum ether (b.p. 77-115°). This compound was prepared earlier by D.F. Pontz, but the analytical results were not confirmatory.

¹Reaction was in ether, and recrystallization was from petroleum ether (b.p. 77-115°). This compound was prepared earlier by D. F. Pontz, but the analytical results for mercury were not confirmatory.

^m This compound was prepared by D. F. Pontz by refluxing in 95% ethanol with two equivalents of NaCN for two hours. The yield was 85.7% and the compound was crystallized either from acetic acid or from 95% ethanol.

ⁿ The compound was crystallized from ethyl acetate and methanol.

^o Recrystallization was from ethyl acetate.

^{*p*} Recrystallization was from petroleum ether (b.p. $30-38^{\circ}$).

^q The recrystallization was first from ethyl acetate and then from petroleum ether (b.p. 60-68°). D. F. Pontz prepared this compound earlier from reaction of octadecylmercuric chloride and bromide with octadecylmagnesium bromide, but his analyses for mercury were not in agreement with the expected R_2Hg compound. He also prepared the compound from *n*-octadecylmercuric bromide and *n*-octadecyllithium. suggested a re-examination of the melting points of hexadecvlmercury chloride, bromide, and iodide which were previously (11) reported as melting at 102°, 101.5°, and 82°, respectively. An article by Rumpf (13) has just been abstracted in Chemical Abstracts on the melting points of some of the RHgX types listed in Table II, and there is good agreement with the values reported. The one exception is the melting point of n-dodecylmercury chloride for which the value of 111.5° is reported.

The melting points reported in Table I for the R₂Hg compounds show a regular gradation with chain length. The relationship may be expressed as $M = 32 + 13\sqrt{n - 11}$ where M is the melting point (Centigrade) and n is the number of carbon atoms in the alkyl group. Incidentally, the dialkylmercury compounds reported are very soluble in petroleum ether and in ether, but very slightly soluble in alcohol.

Organolead compounds. The organolead compounds described in Table III were prepared as indicated. Lead analyses were in accordance with the procedure of Gilman and Robinson (14).

Tetradodecyltin. To 64 cc. of a 0.843 N solution of n-dodecylmagnesium bromide (0.054mole), was added 4.7 g. (0.018 mole) of stannic chloride in 15 cc. of benzene. After refluxing for three and one-half hours, the mixture was hydrolyzed. Recrystallization of the 5.4 g.

R	RHgCl	RHgBr	RHgI
Ethyl	192 (11)	198 (11)	186 (11)
n-Butyl	130 (11)	129.9-130 (10)	117 (11)
n-Hexyl	125 (11)	122.0-122.2 (10)	110 (11)
n-Octyl	115-115.5 (12)	114.8-115.0 (10)	
n-Decyl		111.0-111.4 (10)	_
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	

TABLE II

(45%) of crude material from ether and ethyl acetate removed the tetracosane. The tetradodecyltin melted at 15-16° to a turbid liquid which was clear at 21°; n_{0}^{∞} 1.4692; n_{0}^{∞} 1.4736. Anal. Calc'd for C₄₈H₁₀₀Sn: Sn, 14.91. Found: Sn, 15.18.

The analysis for tin in the several organotin compounds reported here was by the method of Gilman and King (15), and it was found that the use of bromine is not necessary with these relatively non-volatile compounds.

Tetratetradecultin. To 0.087 mole of n-tetradeculmagnesium bromide in ether was added 5.5 g. of stannic chloride. After refluxing for one hour and then standing overnight, the mixture was hydrolyzed, the ether was removed, and the residue was treated with ethyl acetate to dissolve out the R₄Sn compound and leave the octacosane (1.7 g.). The crude tetratetradecyltin (12.7 g. or 66%) was crystallized from ethyl acetate to give 8.6 g. of pure product melting at 33-34°.

Anal. Calc'd for C₅₆H₁₁₆Sn: Sn, 13.07. Found: Sn, 12.92.

Tetrahexadecyltin. To 102 cc. of 0.378 N n-hexadecylmagnesium bromide was added 2.5 g. of stannic chloride in benzene. After the customary procedures, the 7.5 g. (76%)of crude tetrahexadecyltin (m.p. 36-41°), was twice crystallized from ether and melted at 41.5-42.5°.

Anal. Calc'd for C₆₄H₁₃₂Sn: Sn, 11.63. Found: Sn, 11.84.

Tetraoctade cyltin. From a reaction between n-octade cylmagnesium bromide (0.0392 mole) and stannic chloride (0.0087 mole) was obtained 5.6 g. (56.8%) of pure tetraoctadecyltin which melted at 47° after being crystallized three times from ethyl acetate.

Anal. Calc'd for C₇₂H₁₄₈Sn: Sn, 10.48. Found: Sn, 10.36.

Tridodecyltin chloride. An ethereal solution of tetradodecyltin was saturated with dry hydrogen chloride; the tube was then stoppered and set aside overnight. Recrystallization from ethyl acetate and methanol, and then from ether-ethanol gave crystals melting at 33°.

REACTANTS	PRODIICT	M.P. °C	anal. % Pb	
			Calc'd	Found
$n-C_{12}H_{25}MgBr + PbCl_2$	$(C_{12}H_{25})_{3}PbCl^{a}$	63.5	27.60	27.46
$(C_{12}H_{25})_{3}PbCl + AgNO_{3}$	$(C_{12}H_{25})_{3}PbNO_{3}^{b}$	44 - 45	26.66	26.98
$(C_{12}H_{25})_{3}PbCl + AgOAc$	$(C_{12}H_{25})_{3}PbOAc$ $^{\circ}$	59	26.76	26.90
$n-C_{14}H_{29}MgBr + PbCl_2$	$(C_{14}H_{29})_{3}PbCl^{d}$	74-75	24.8	24.8
$n-C_{16}H_{33}MgCl + PbCl_2$	$(C_{16}H_{33})_{3}PbCl^{e}$	7980	22.55	22.67
$n-C_{18}H_{37}MgBr + PbCl_2$	(C ₁₈ H ₃₇ PbCl ¹	82-83	20.66	20.71
$(C_{14}H_{29})_{3}PbCl + C_{14}H_{29}MgBr$	$(C_{14}H_{29})_4Pb^{g}$	31	20.78	20.92
$(C_{16}H_{33})_{3}PbCl + C_{16}H_{33}MgBr$	$(\mathrm{C}_{16}\mathrm{H}_{33})_4\mathrm{Pb}^{\hbar}$	42	18.68	18.56

TABLE III

ORGANOLEAD COMPOUNDS

^a The compound was purified by recrystallization from ethyl acetate. In order to establish more definitely that the product was tridodecyllead *chloride* and not the bromide, a synthesis was carried out using dodecylmagnesium *chloride* and lead chloride. The product of this reaction melted at $64-65^{\circ}$, and a mixed m.p. with the product obtained by starting with *n*-dodecylmagnesium bromide was $63-64^{\circ}$.

^b The reaction was carried out in absolute ethanol, and crystallization was from ethyl acetate.

^c Reaction was effected in 95% ethanol, and the product crystallized out on cooling.

^d A first crystallization from petroleum ether left a yellow insoluble solid which may have been some R_3Pb compound. Final crystallization from ethyl acetate raised the m.p. one degree to 74–75°. A chlorine analysis by the Parr bomb procedure gave a low analysis: Calc'd, Cl, 4.25; Found, 2.48. Chlorine analyses of some organometallic compounds by this procedure are often low.

^e The solids obtained after hydrolysis by ammonium chloride solution were first extracted (Soxhlet) with chloroform. The product obtained from the chloroform solution was first crystallized from ethyl acetate and then from petroleum ether.

^f The Grignard reagent was filtered as usual, and this served to remove most of the coupling product (hexatriacontane). The hexatriacontane was then washed free of Grignard reagent by ether. Crystallization of the R_3PbCl product was first done with ethyl acetate and then with petroleum ether.

^o Crystallization was from ethyl acetate and then from ether.

^A To effect separation from R_3 PbCl, the product was suspended in petroleum ether, cooled in ice, and filtered; then the filtrate was treated with methanol and ethyl acetate to obtain the R₄Pb compound which melted at this stage at 39-42°. Recrystallization from petroleum ether gave the sharp m.p. 42°. It is interesting to note that the molecular weight of this organometallic compound is 1107.

Anal. Calc'd for C₃₆H₇₅ClSn: Sn, 17.93. Found: Sn, 17.73.

Tritetradecyltin chloride. Attempts to cleave tetratetradecyltin in (a) petroleum ether with dry hydrogen chloride, and (b) with stannic chloride in benzene gave unchanged R4Sn compound.

Cleavage of 3.6 g. of tetradecyltin in dry ether with dry hydrogen chloride gave, after

standing for 6 hours, 2.6 g. (85%) of tritetradecyltin chloride, melting at 46-47°. Recrystallization from ethyl acetate did not change the melting point.

Anal. Cale'd for $C_{42}H_{87}ClSn: Sn, 15.91$. Found: Sn, 15.29.

Trihexadecyltin chloride. The product obtained by saturating an ether solution of 2.1 g. (0.002 mole) of tetrahexadecyltin with hydrogen chloride at room temperature was crystallized from ethyl acetate to give 1.27 g. (74%) of trihexadecyltin chloride, melting at 55.5-56.5°.

Anal. Calc'd for C48H99ClSn: Sn, 1430. Found: Sn, 14.75.

Trioctadecyltin chloride. From an ether solution of 2.2 g. (0.00194 mole) of tetraoctadecyltin which was saturated with hydrogen chloride and then set aside overnight was obtained 1.1 g. (62%) of trioctadecyltin chloride, melting at 61-62° after crystallizing from ethyl acetate and then from ether.

Anal. Calc'd for C₅₄H₁₁₁ClSn: Sn, 12.98. Found: Sn, 12.86.

Tri-n-dodecylarsenic. To an ether solution of n-dodecylmagnesium bromide (prepared from 0.082 mole of n-dodecyl bromide) was added slowly a solution of 7.85 g. (0.0249 mole) of arsenic tribromide in 20 cc. of ether. Two liquid layers separated, the upper brown, and the lower colorless. After hydrolysis by aqueous ammonium chloride, and drying by

A	M.P.,°C	В	м .₽., °С.	а+вм.р. °С.
C ₁₂ H ₂₅ HgBr	108-108.7	C14H29HgBr	110-110.5	102-103
C ₁₆ H ₃₃ HgBr	110.5-111.5	$C_{18}H_{37}HgBr$	110-111	107-109
$(C_{16}H_{33})_{2}Hg$	61-62	$(C_{18}H_{37})_{2}Hg$	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	C18H37HgBr	110-111	109-110
$C_{12}H_{25}HgI$	91	$C_{16}H_{33}HgI$	93-93.5	83-84
C ₁₆ H ₃₈ HgBr	110.5-111.5	$C_{16}H_{33}HgI$	93-93.5	92 - 95
$(C_{12}H_{25})_{3}PbCl$	64 - 65	(C14H29)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	$(C_{18}H_{37})_{3}SnCl$	61-62	56-57
$(C_{16}H_{33})_4Sn$	41.5 - 42.5	$(C_{16}H_{33})_3SnCl$	55.5 - 56.5	52 - 55
$(C_{16}H_{83})_4Sn$	41.5 - 42.5	$(C_{13}H_{37})_4Sn$	47	42-47

TABLE IV Mixed Melting Points

sodium sulfate, the ether was removed by distillation in a stream of dry nitrogen. The 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 much in the subsequent distillation.

Distillation was carried out in an all-glass apparatus. The tri-*n*-dodecylarsenic distilled at about $220^{\circ}/0.08$ mm. or $200^{\circ}/0.009$ mm. with the bath at 308° ; the yield was 8.12 g. or 56%. Analysis for arsenic was by the method of Tabern and Shellberg (9).

Anal. Calc'd for C₃₆H₇₅As: As, 12.85. Found: As, 12.41.

From the values d_{20}^{35} 0.900 and $n_{\rm D}^{35}$ 1.4740, the molecular refraction is 180.6 (calculated, 181.51).

Tri-n-tetradecylarsenic. The reaction for this preparation was carried out between *n*-tetradecylmagnesium bromide and arsenic tribromide (0.024 mole), by operations like those described above.

On distillation, tetradecane was collected at $70^{\circ}/0.22$ mm., and octacosane at 150–160°/0.0008 mm. Then as the temperature was raised there was slight fuming followed by a sudden rapid distillation of liquid and a deposition of a black solid on the neck of the Claisen flask. 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.

Anal. Calc'd for $(C_{14}H_{29})_3As$: As, 11.22. Found: for distillate, As, 8.6; for residue, As, 11.19.

From these constants on the residue, d_{20}^{35} 0.908 and n_D^{35} 1.4740, the molecular refraction is 206.4 (calculated, 209.26).

Mixed melting points. 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 IV.

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SUMMARY

A series of long-chained organometallic compounds with lithium, sodium, potassium, calcium, mercury, arsenic, tin, and lead has been prepared. Some of their properties and relationships (particularly melting points) have been noted.

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