Summary

Hitherto inaccessible secondary and tertiary alkyllithium compounds can now be obtained by direct reaction of alkyl chlorides and lithium in low-boiling petroleum ether.

The relative effectiveness of a series of alkyllithium compounds for metalation and for halogen–metal interconversion reactions in different solvents has been examined.

AMES, IOWA
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Preferential Cleavage of Radicals in Some Organometallic Compounds[1]

BY HENRY GILMAN, FRED W. MOORE AND R. G. JONES

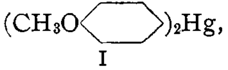
The primary objective in this study was the introduction of water-solubilizing groups into some relatively unreactive organometallic compounds. Two ways suggested themselves. The first was a nuclear metalation, followed by carbonation, as a means of inserting the water-solubilizing carboxyl group.

$$R_3PbC_6H_5 \xrightarrow{R'Li} R_3PbC_6H_4Li \xrightarrow[(HOH)]{(CO_2)} R_3PbC_6H_4CO_2H$$

Second, halogen–metal interconversion reactions were examined.

$$R_3PbC_6H_4Br\text{-}p \xrightarrow{R'Li} R_3PbC_6H_4Li\text{-}p \xrightarrow[(HOH)]{(CO_2)} R_3PbC_6H_4CO_2H\text{-}p$$

Both reactions were unsatisfactory because metal–metal interconversions took place more rapidly than either metalation or halogen–metal interconversion.

From earlier work it was to be expected that the speed of a halogen–metal interconversion reaction would be greatest if iodine were the nuclear halogen and that this speed would be further enhanced by having the iodine ortho to an activating alkoxy group. A compound like *bis*-(3-iodo-4-methoxyphenyl)mercury,  gave promise of satisfying the essential conditions. The compound was synthesized by reactions described in the experimental part and, when treated with *n*-butyllithium followed by carbonation, actually yielded an organomercury compound containing a carboxyl group. However, even in this case and with only a two-minute period of reaction, the metal–metal interconversion was appreciable. This general approach may prove more satisfactory with RM compounds that undergo the M–M interconversion less readily such as those of germanium, but it now appears that the reaction is of little promise because M–M interconversions proceed much more rapidly than metalation and appreciably faster than X–M interconversions.

Preferential Cleavage of Radicals.—As an outgrowth of the afore-mentioned objective, a study was made of the rates of M–M interconversion of some symmetrical and unsymmetrical organometallic compounds of lead, tin and mercury. An illustrative reaction with an unsymmetrical compound is

$$(C_6H_5)_2Pb(C_6H_4Cl\text{-}p)_2 + n\text{-}C_4H_9Li \xrightarrow[(HOH)]{(CO_2)} \begin{cases} C_6H_5CO_2H \\ p\text{-}ClC_6H_4CO_2H \end{cases}$$

Using one-half an equivalent of *n*-butyllithium it was observed that the acids formed on carbonation of the reaction mixture consisted of a mixture of 98% *p*-chlorobenzoic acid and 2% benzoic acid. That is, the *p*-chlorophenyl radical was cleaved much more rapidly than the phenyl radical.

As was the case in a recently reported study on organobismuth compounds,[2] the series formulated by placing the organic radicals in the order of decreasing ease of cleavage from organolead compounds by means of *n*-butyllithium does not agree with similar series based upon cleavage of RM compounds with other cleaving agents. Furthermore, there were sufficient variations in the bismuth, tin, lead and mercury series, using the same cleaving agent (*n*-butyllithium), to emphasize the importance not only of the radicals and the cleaving agent, but, also, of the central metallic element.

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[1] Paper XLII in the series: "Relative reactivities of organometallic compounds"; the preceding paper is Gilman, Moore and Baine, THIS JOURNAL, 63, 2479 (1941).

[2] Gilman and Yale, *ibid.*, 63, in press (1941).

Relative Reactivities of RM Compounds.—A miscellany of reactions has indicated that organotin compounds are less reactive than the corresponding organolead compounds. However, we now find that in a M–M interconversion reaction with *n*-butyllithium there is only a 30% cleavage of tetraphenyllead under conditions where tetraphenyltin is cleaved to the extent of 45%. Steric factors may be partly responsible for the 3% cleavage of tetra-*o*-tolyllead under the same conditions, for an earlier study[3] showed that tetra-*p*-tolyllead was cleaved more rapidly than tetraphenyllead under similar conditions and that the *p*-tolyl radical was cleaved more rapidly than the phenyl radical from diphenyldi-*p*-tolyllead.

Relative Effectiveness of RLi Compounds in M–M Interconversions.—In the preceding paper[1] a comparison was made of the relative effectiveness of RLi compounds in metalation and in halogen–metal interconversion reactions. On the basis of present findings, the order of decreasing effectiveness of some RLi compounds in the M–M interconversion reaction with tetraphenyllead is: C_2H_5Li, n-C_3H_7Li, n-C_4H_9Li, CH_3Li, $C_6H_5C{\equiv}CLi$. With tetra-*p*-chlorophenyltin the order in diethyl ether is: n-C_4H_9Li, (CH_3Li, C_6H_5Li); and in petroleum ether, (n-C_4H_9Li, i-C_4H_9Li, s-C_4H_9Li), t-C_4H_9Li.

The low effectiveness of $C_6H_5C{\equiv}CLi$ is in agreement with the generally low reactivity of practically all types of $RC{\equiv}CM$ compounds. The relatively low effectiveness of CH_3Li is paralleled by its low reactivity in metalation and X–M interconversion reactions, as well as many other reactions such as ether cleavage. It is particularly interesting to note that *t*-butyllithium is relatively low in reactivity in the M–M interconversion, but high in reactivity in metalation and X–M interconversion. The absence of a M–M interconversion between tetra-*p*-chlorophenyltin and *t*-butyllithium is noteworthy, for the *p*-chlorophenyl radical is generally cleaved with great ease in reactions with RLi compounds.

Experimental

The results of a series of metal–metal interconversion reactions are given in Table I. Unless noted otherwise the mixtures were stirred at room temperature and the yields of RCO_2H are calculated on the basis of total cleavage of RM.

Triphenyl-*p*-chlorophenyllead and Diphenyldi-*p*-chlorophenyllead with *n*-Butyllithium.—To 0.004 mole of each of the organolead compounds in 65 ml. of ether was added 0.004 mole of *n*-butyllithium in 10 ml. of ether. The solutions were stirred for ten minutes and then carbonated. The compositions of the resulting acid mixtures, as determined from neutralization data, were

Triphenyl-*p*-chlorophenyllead: $C_6H_5CO_2H$, 24%; *p*-$ClC_6H_4CO_2H$, 76%.

Diphenyldi-*p*-chlorophenyllead: $C_6H_5CO_2H$, 2%; *p*-$ClC_6H_4CO_2H$, 98%.

Triphenyl-*p*-bromophenyllead and RLi Compounds.—To a benzene–petroleum ether solution of 0.007 mole of triphenyl-*p*-bromophenyllead was added 0.015 mole of *t*-butyllithium in petroleum ether. The solution was stirred at room temperature, and after fifteen minutes and also one hour aliquots were removed, carbonated and hydrolyzed. No lead-containing acid was obtained.

In other experiments, *s*-butyllithium was used. Here, also, no lead-containing acid was isolated, and the recovery of triphenyl-*p*-bromophenyllead averaged above 90%.

***bis*(3-Iodo-4-methoxyphenyl)-mercury.**—Reduction of 2-iodo-4-nitroanisole by stannous chloride in 95% ethanol gave a 70% yield of 3-iodo-4-methoxyaniline which melted at 73–74° after crystallization from petroleum ether (b. p. 60–68°).[4] A suspension of 20 g. (0.07 mole) of 3-iodo-4-methoxyaniline hydrochloride was diazotized, and the diazonium chloride–mercuric chloride double salt was formed in the customary manner.[5] The double salt, which melted with decomposition sharply at 145°, appeared to be uncommonly stable. A sample for analysis was heated above 100° with concd. sulfuric acid before any decomposition appeared to take place and then charring occurred. The volume of gas liberated was much in excess of the calculated quantity.

After decomposing the double salt with copper powder in acetone and treating the mixture with concd. ammonium hydroxide, the solid residue was filtered, dried and extracted with chloroform. The buff-colored crystalline powder from the chloroform extraction was boiled in ethanol for three hours with a little hydrazine hydrate.[6] The dry residue from this treatment was extracted with chloroform to give a light-brown crystalline powder. Chloroform extraction was very slow because of the great insolubility of the compound which softened at 250° and melted with decomposition at 253–254°.

Anal.[7] Calcd. for $C_{14}H_{12}O_2I_2Hg$: Hg, 30.10. Found: Hg, 30.43.

Reaction of *bis*-(3-Iodo-4-methoxyphenyl)-mercury with *n*-Butyllithium.—To a suspension of 2.45 g. (0.0037 mole) of the mercurial in 40 ml. of ether was added quickly, and with stirring, 10 ml. of 0.88 molar (0.0088 mole) of *n*-butyllithium. After stirring two minutes at room temperature, the mixture was carbonated with solid carbon dioxide. The carbonation mixture was treated with water, and 0.95 g. of the mercurial was recovered (mixed m. p.).

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(3) Gilman and Moore, THIS JOURNAL, **62**, 3206 (1940). On the basis of the generally anomalous cleavage reactions with *n*-butyllithium, it is doubtful if the M–M interconversion reaction has much validity in comparing the relative reactivities of R_6Pb_2 and R_4Pb types. Furthermore, Mr. E. Bindschadler has shown that *n*-butyllithium first cleaves an R_6Pb_2 compound to give R_3PbLi and $R_3PbC_4H_9$-*n*.

(4) Reverdin, *Ber.*, **29**, 997 (1896), reports a m. p. of 74–75°.

(5) Nesmejanow and Kahn, *ibid.*, **62**, 1018 (1929).

(6) Gilman and Barnett, *Rec. trav. chim.*, **55**, 563 (1936).

(7) Analysis was made by the method of Tabern and Shellberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 401 (1932).

TABLE I

METAL–METAL INTERCONVERISONS

	RM	R'M'	Reaction time, hr.	Medium	RCO_2H	(%)
1	$(C_6H_5)_4Pb$	CH_3Li[a]	15	$(C_2H_5)_2O$	$C_6H_5CO_2H$	(40)
2	$(C_6H_5)_4Pb$	C_2H_5Li[b]	0.5	$(C_2H_5)_2O$	$C_6H_5CO_2H$	(45)
3	$(C_6H_5)_4Pb$	C_2H_5Li[b]	7	$(C_2H_5)_2O$	$C_6H_5CO_2H$	(65)
4	$(C_6H_5)_4Pb$	n-C_3H_7Li[b]	0.5	$(C_2H_5)_2O$	$C_6H_5CO_2H$	(40)
5	$(C_6H_5)_4Pb$	n-C_3H_7Li[b]	7	$(C_2H_5)_2O$	$C_6H_5CO_2H$	(59)
6	$(C_6H_5)_4Pb$	n-C_4H_9Li[b]	0.5	$(C_2H_5)_2O$	$C_6H_5CO_2H$	(38)
7	$(C_6H_5)_4Pb$	n-C_4H_9Li[b]	7	$(C_2H_5)_2O$	$C_6H_5CO_2H$	(54)
8	$(C_6H_5)_4Pb$	$C_6H_5C{\equiv}CLi$[c]	67	$(C_2H_5)_2O$	$C_6H_5CO_2H$	(0)
9	$(C_6H_5)_4Pb$	n-C_4H_9Na[d]	2	Pet. ether (b. p. 85–100°)	$C_6H_5CO_2H$	(19)
10	$(C_6H_5)_4Pb$	n-C_4H_9Na[d]	8	Pet. ether (b. p. 85–100°)	$C_6H_5CO_2H$	(25)
11	$(C_2H_5)_4Pb$	C_6H_5Li[e]	12	$(C_2H_5)_2O$	$C_2H_5CO_2H$	(0)
12	$(C_6H_5)_4Sn$	n-C_4H_9Li[f]	24	$(C_2H_5)_2O$-C_6H_6	$C_6H_5CO_2H$	(36)
13	$(C_6H_5)_4Sn$	n-C_4H_9Li[f]	48	$(C_2H_5)_2O$-C_6H_6	$C_6H_5CO_2H$	(21)
14	$(C_6H_5)_4Sn$	$C_6H_5CH_2Na$[g]	24	C_7H_8	$C_6H_5CO_2H$	(0)
15	$(p$-$ClC_6H_4)_4Sn$	CH_3Li[h]	0.25	$(C_2H_5)_2O$	p-$ClC_6H_4CO_2H$	(55)
16	$(p$-$ClC_6H_4)_4Sn$	n-C_4H_9Li[i]	0.16	$(C_2H_5)_2O$	p-$ClC_6H_4CO_2H$	(72)
17	$(p$-$ClC_6H_4)_4Sn$	n-C_4H_9Li[i,j]	4	C_6H_6-, pet. ether	p-$ClC_6H_4CO_2H$	(40)
18	$(p$-$ClC_6H_4)_4Sn$	n-C_4H_9Li[k]	0.5	Pet. ether (b. p. 28–38°)	p-$ClC_6H_4CO_2H$	(6)
19	$(p$-$ClC_6H_4)_4Sn$	n-C_4H_9Li	4	Pet. ether (b. p. 28–38°)	p-$ClC_6H_4CO_2H$	(26)
20	$(p$-$ClC_6H_4)_4Sn$	i-C_4H_9Li	0.5	Pet. ether (b. p. 28–38°)	p-$ClC_6H_4CO_2H$	(8)
21	$(p$-$ClC_6H_4)_4Sn$	i-C_4H_9Li	4	Pet. ether (b. p. 28–38°)	p-$ClC_6H_4CO_2H$	(19)
22	$(p$-$ClC_6H_4)_4Sn$	s-C_4H_9Li	0.5	Pet. ether (b. p. 28–38°)	p-$ClC_6H_4CO_2H$	(5)
23	$(p$-$ClC_6H_4)_4Sn$	s-C_4H_9Li	4	Pet. ether (b. p. 28–38°)	p-$ClC_6H_4CO_2H$	(22)
24	$(p$-$ClC_6H_4)_4Sn$	t-C_4H_9Li	4	Pet. ether (b. p. 28–38°)	p-$ClC_6H_4CO_2H$	(0)
25	$(p$-$ClC_6H_4)_4Sn$	C_6H_5Li	0.25	$(C_2H_5)_2O$	p-$ClC_6H_4CO_2H$	(53)
26	$(C_6H_5)_2Hg$	n-C_4H_9Li[l]	.03	C_6H_6–pet. ether	$C_6H_5CO_2H$	(65)
27	$(C_6H_5)_2Hg$	n-C_4H_9Li[l]	.25	C_6H_6–pet. ether	$C_6H_5CO_2H$	(62)
28	$(C_6H_5)_2Hg$	t-C_4H_9Li	.03	C_6H_6–pet. ether	$C_6H_5CO_2H$	(10)
29	$(C_6H_5)_2Hg$	t-C_4H_9Li	.25	C_6H_6–pet. ether	$C_6H_5CO_2H$	(13)
30	$(C_6H_5CH_2)_2Hg$	n-C_4H_9Li[l]	.03	C_6H_6–pet. ether	$C_6H_5CH_2CO_2H$	(53)
31	$(C_6H_5CH_2)_2Hg$	n-C_4H_9Li[l]	.25	C_6H_6–pet. ether	$C_6H_5CH_2CO_2H$	(40)
32	$(C_6H_5CH_2)_2Hg$	t-C_4H_9Li	.03	C_6H_6–pet. ether	$C_6H_5CH_2CO_2H$	(15)
33	$(C_6H_5CH_2)_2Hg$	t-C_4H_9Li	.25	C_6H_6–pet. ether	$C_6H_5CH_2CO_2H$	(15)
34	$(C_6H_5CH_2)_2Hg$	CH_3Li[m]	.008	$(C_2H_5)_2O$	$C_6H_5CH_2CO_2H$	(79)
35	$(C_6H_5CH_2)_2Hg$	CH_3Li_m	.5	$(C_2H_5)_2O$	$C_6H_5CH_2CO_2H$	(73)

[a] No benzoic acid was isolated from an aliquot which was removed and carbonated at the end of three hours. A solution of 0.54 mole of methyllithium was mixed with 0.0126 mole of $(C_6H_5)_4Pb$. [b] To 0.06 mole of RLi compound was added 0.0146 mole of finely powdered $(C_6H_5)_4Pb$. [c] Aliquots were removed and carbonated at several intervals prior to sixty-seven hours and no benzoic acid was isolated. The recovery of $(C_6H_5)_4Pb$ was 87%. [d] The removal of aliquots from the suspension was rather difficult and, for this reason, the yields are only approximate. Under these conditions $(C_6H_5)_4Pb$ is not appreciably affected by sodium metal. [e] The recovery of $(C_2H_5)_4Pb$ was 95%. [f] A solution of 0.05 mole of n-butyllithium in ether was added to 0.003 mole of $(C_6H_5)_4Sn$ in benzene and the mixture was refluxed (55°). The yield of $(n$-$C_4H_9)_4Sn$ in Expt. 12 was 81% and in Expt. 13 was 88% indicating a greater interconversion than shown by the acid yields. Using benzene alone as solvent only a trace of benzoic acid was isolated, while in pet. ether (b. p. 85–100°) no benzoic acid was isolated. [g] From this experiment 90% of the $(C_6H_5)_4Pb$ was recovered. The benzylsodium was prepared from chlorobenzene, sodium and toluene [Gilman, Pacevitz and Baine, THIS JOURNAL, **62,** 1514 (1940)]. [h] A solution of 0.02 mole of methyllithium was mixed with 0.005 mole of $(p$-$ClC_6H_4)_4Sn$. [i] The solution contained 0.004 mole of R_4Sn compound and 0.004 mole of n-butyllithium. The yield of acid is based on the removal of one p-chlorophenyl group. [j] The yield is based on the removal of one p-chlorophenyl group. After eight hours of reaction the yield was 45%. [k] In Expts. 18–25, a solution of 0.02 mole of the RLi compound in 200 ml. of solvent was mixed with 0.005 mole of the R_4Sn compound. [l] A solution of 0.005 mole of R_2Hg in 150 ml. of benzene was mixed with 0.01 mole of RLi compound in 50 ml. of pet. ether (b. p. 28–38°). [m] A solution of 0.02 mole of methyllithium and 0.01 mole of R_2Hg in 300 ml. of ether.

The ether solution was treated with 2 g. of mercuric chloride,[8] and 0.5 g. (0.0017 mole) n-butylmercuric chloride (m. p. 120–122°, and mixed m. p. 122–124°) was isolated.

The aqueous extract of the carbonation mixture gave an insoluble acid on acidification with hydrochloric acid. Part of this acid was dissolved in dilute sodium hydroxide; the solution was boiled with Norite, then filtered and acidi-

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[8] To convert any di-n-butylmercury formed by an M–M interconversion reaction to the solid n-butylmercuric chloride which melts at 126°.

fied to give a mercury-containing acid which melted between 250–260°, had a neutralization equivalent of 190, and was completely soluble in sodium bicarbonate solution. The small quantity of product was undoubtedly admixed with some of the coupling product and some of the mercury-acid formed by a mono- X–M interconversion reaction.

Summary

A series of metal–metal interconversion reactions has been carried out between organometallic compounds of lead, tin and mercury and RLi compounds in different media.

The cleavage series of radicals does not agree with the series based on the hydrogen chloride cleavage of unsymmetrical RM compounds, and also varies somewhat with the kind of central metallic atom. Tetraphenyltin is cleaved more rapidly by *n*-butyllithium than is tetraphenyllead. Generalizations have been formulated on the relative effectiveness of some RLi compounds in metal–metal interconversions.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

N-Benzylphenylhydroxylamine

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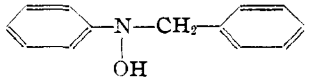
The alkylarylhydroxylamines constitute a group of compounds whose reactions have received very little study. Since Vavon and Crajcinovic[1] had shown that benzylphenylhydroxylamine (I) could



I

be prepared readily by the partial reduction of a mixture of nitrobenzene and benzaldehyde, we selected this representative as the most convenient member of the series to study.

Benzylphenylhydroxylamine is basic, forming readily crystallizable salts. The hydroxyl group is easily benzoylated. When the compound is treated with bromine in carbon tetrachloride, a bromine atom is introduced para to the hydroxylamino group. This was shown by reducing the benzyl-*p*-bromophenylhydroxylamine so obtained to benzyl-*p*-bromoaniline.

The reaction with sulfuric acid was of especial interest since both the hydroxyl group in phenylhydroxylamines and the alkyl group in alkylanilines are known to migrate to the para position. However, in this case the acid first dealkylated the hydroxylamine. When 20% acid was used, derivatives of phenylhydroxylamine were isolated. With more dilute acid (5%) rearrangement occurred, so that *p*-aminophenol was obtained as the product of the reaction.

Experimental

N-Benzylphenylhydroxylamine was prepared by the method of Vavon and Crajcinovic.[1]

The hydrochloride, prepared by passing hydrogen chloride through an ether solution of the hydroxylamine, was crystallized from a mixture of alcohol and ether, m. p. 104–105°.

Anal. Calcd. for $C_{13}H_{14}ONCl$: Cl, 15.1. Found: Cl, 15.1.

The hydrobromide, prepared by the same method, was crystallized from absolute alcohol and ether, m. p. 96–97°.

Anal. Calcd. for $C_{13}H_{14}ONBr$: N, 5.00. Found: N, 4.94.

The benzoyl derivative also was prepared. It crystallized from aqueous alcohol, m. p. 115–117°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: N, 4.62. Found: N, 4.55, 4.70.

N-Benzyl-*p*-bromophenylhydroxylamine.—To a solution of 5 g. of benzylphenylhydroxylamine in 100 cc. of carbon tetrachloride was added a solution of 4 g. of bromine in 40 cc. of carbon tetrachloride. The dark red oil, which first precipitated, slowly crystallized when cooled. It was filtered and recrystallized from aqueous alcohol, m. p. 164–165°, yield 4 g. (56%).

Anal. Calcd. for $C_{13}H_{12}ONBr$: N, 5.04. Found: N, 5.19.

N-Benzyl-*p*-bromoaniline was prepared by reducing the benzyl-*p*-bromophenylhydroxylamine with low pressure hydrogen in the presence of platinum. It melted at 53–54° (55°),[2] after one crystallization from alcohol.

Phenylhydroxylamine.—When 3 g. of benzylphenylhydroxylamine was added to 10 cc. of concentrated sulfuric acid and 40 g. of ice and the resulting mixture boiled for fifteen minutes, a white crystalline solid separated on cooling. This solid, which decomposed at 221–223° and was insoluble in hot alcohol, weighed 2.8 g. When it was treated with benzoyl chloride, N-benzoylphenylhydroxylamine was obtained, m. p. 123–124° (123–124°).[3] Likewise treatment with acetic anhydride yielded N-acetylphenylhydroxylamine, m. p. 67–68° (67.0–67.5°).[4]

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[1] Vavon and Crajcinovic, *Compt. rend.*, **187**, 420 (1928).

[2] Dains and Eberly, THIS JOURNAL, **55**, 3859 (1933).

[3] Ciamician and Silber, *Gazz. chim. ital.*, **36**, II, 172 (1906).

[4] Bamberger and Destraz, *Ber.*, **35**, 1874 (1902).