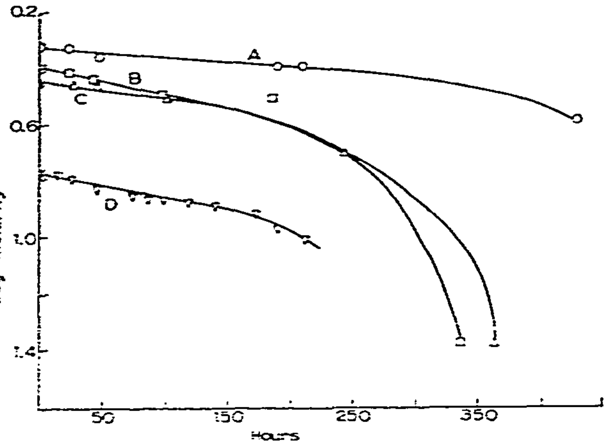
SHORT COMMUNICATIONS

Relative reactivities of organic group IVB lithium compounds

II*. Stability in tetrahydrofuran

The reaction of triphenylsilyllithium with tetrahydrofuran has been investigated previously[1], and the product, formed in good yield, is 4-(triphenylsilyl)-1-butanol. The stabilities of triphenyl-, methyldiphenyl- and dimethylphenylsilyllithium have also been measured[2] by analyzing for silyllithium content at various time intervals. The method of analysis employed consisted of decomposition of the silyllithium reagent with *n*-butyl bromide followed by determination of bromide ion by Volhard titration[2]. In the present work the stabilities of the additional lithium reagents listed in Table 1 have been measured using the method of double titration with allyl bromide[3]. These data were given a kinetic treatment to determine the rates of reaction with tetrahydrofuran.



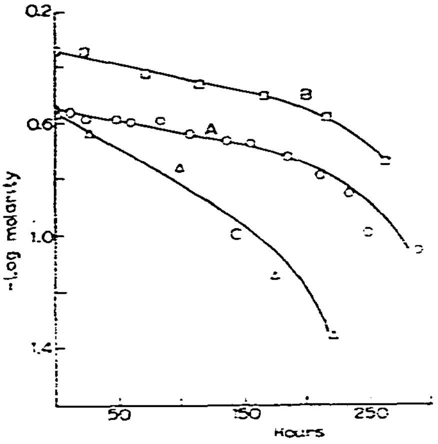


Fig. 1. —Log molarity *vs.* time for triphenylsilyllithium (A), methyldiphenylsilyllithium (B), dimethylphenylsilyllithium (C), and triphenylgermyllithium (D) at room temperature in tetrahydrofuran.

Fig. 2. —Log molarity *vs.* time for triphenyltinlithium (A), methyldiphenyltinlithium (B), and tri-*n*-butyltinlithium (C) at room temperature in tetrahydrofuran.

In Figs. 1 and 2, the logarithm of molarity is plotted against time. It will be noted that the decompositions follow pseudo first order kinetics only through the first part of the reaction. In all cases the rate is accelerated, possibly by a catalytic effect of one of the reaction products, until the deviation from first order kinetics is quite extreme. In Table 1 the first order rate constants for the reactions are given. The constants were determined using the initial linear portions of the curves in Figs. 1 and 2.

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* For Part I, see ref. 5.

TABLE 1

REACTIONS OF GROUP IVB LITHIUM COMPOUNDS WITH TETRAHYDROFURAN

Reagent	$k_1 \times 10^3$ *hours*$^{-1}$
Ph_3SiLi	0.84
$Ph_2MeSiLi$	2.1
$PhMe_2SiLi$	1.4
Ph_3GeLi	1.8
Ph_3SnLi	1.8
$Ph_2MeSnLi$	2.3
n-Bu_3SnLi	5.9

Among the silyllithium reagents it will be noted that the rate of decomposition of methyldiphenylsilyllithium is greater than that of dimethylphenylsilyllithium, in agreement with the relative reactivities observed in chloride displacement from *n*-butyl chloride[4] and in metalation of fluorene[5]. Among the tinlithium reagents one observes the expected increase in rate on substitution of alkyl groups for aryl groups on the tin atom; however, dimethylphenyltinlithium has not yet been studied.

A rather interesting result is that triphenylgermyllithium and triphenyltinlithium react faster than triphenylsilyllithium, an order that is not in agreement with the relative nucleophilicities of the reagents as shown in chloride displacement[4]. Unfortunately it is not known at present whether the reactions have the same mechanism, or even whether the same type of product is formed. Thus, a rationalization of the observed reactivity sequence seems premature at present.

Experimental

Triphenylgermyllithium[6], triphenyltinlithium[7] and tri-*n*-butyltinlithium* were prepared according to published procedures in tetrahydrofuran solution. The tetrahydrofuran was purified by refluxing over sodium wire, distillation into lithium aluminum hydride, and distillation from the hydride immediately before use. Stabilities were measured by removing aliquots of the solutions at various time intervals and analyzing for the lithium reagent by double titration with allyl bromide[3]. The solutions were kept at room temperature under nitrogen atmosphere during the period that titrations were made.

Preparation of methyldiphenyltin chloride. To a solution of 72.8 g (0.20 mole) of methyltriphenyltin in 350 ml of chloroform heated to reflux temperature was added dropwise a solution of 50.5 g (0.20 mole) of iodine in one l of chloroform. The purple iodine color was discharged rapidly at first, then more slowly, until 1 h was required for the color to fade at the end of the addition. The solvent was evaporated and the resulting oil taken up in ether. The ether solution was extracted three times with 20 % sodium hydroxide, once with distilled water, and three times with 10 % hydrochloric acid. The ether layer was dried over sodium sulfate and the solvent evaporated to leave an oil which was distilled at reduced pressure to obtain impure methyldiphenyltin chloride, b.p. 137–150°/0.5 mm. Redistillation afforded 29.4 g (44.2 %) of the pure product, b.p. 129–130°/0.15 mm, n_D^{20} 1.6140. (Found: C, 48.59, 48.55; H, 4.16, 4.20; Cl, 11.2, 11.0. $C_{13}H_{13}ClSn$ calcd.: C, 48.28; H, 4.05; Cl, 11.0 %.)

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* Tri-*n*-butyltinlithium was prepared as in ref. 3. See also ref. 8.

From the residue of the first distillation was obtained a solid which was recrystallized from dry petroleum ether (b.p. 60–70°) to give 2.4 g (3.1 %) of triphenyltin chloride, m.p. 101–103° (mixed m.p. 103–105°).

Preparation of methyldiphenyltinlithium. To 7.9 g (0.024 mole) of methyldiphenyltin chloride and 0.52 g (0.075 g-atom) of finely cut lithium wire was added a small amount of tetrahydrofuran. Stirring was commenced, and an immediate exothermic reaction took place. Tetrahydrofuran (50 ml) was added, and the mixture rapidly became green-brown in color. After stirring for 3 h, titration showed a 93.7 % yield of the tinlithium reagent.

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Chemistry Department, Iowa State University,
Ames, Iowa (U.S.A.)

HENRY GILMAN
FRANK K. CARTLEDGE
SEE-YUEN SIM

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An electrolytic preparation of methylaluminium diiodide

Methyl aluminium diiodide can be prepared by the reaction

$$3CH_3I + 2Al \longrightarrow (CH_3)_2AlI + CH_3AlI_2$$

but attempts to isolate the diiodide have proved very difficult; fractional distillation under reduced pressure have resulted in complete disproportionation of the diiodide[1].

$$2CH_3AlI_2 \longrightarrow (CH_3)_2AlI + AlI_3$$

The diiodide has been prepared by the following method[1]. The monoiodide was melted with aluminium triiodide at 170°.

$$(CH_3)_2AlI + AlI_3 \longrightarrow 2CH_3AlI_2$$

This was followed by fractional distillation under reduced pressure to remove the diiodide from the reaction mixture (considerable disproportionation occurred at this stage). The pure compound was obtained by repeated recrystallization from *n*-pentane.