

ized are soluble and partially fusible as a consequence of their predominantly linear chain structure. Future work will involve a study of the crosslinking behavior of these products, utilizing the highly nucleophilic character of the methoxy-substituted phenyl side-groups.

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SHORT COMMUNICATIONS

Stabilities of some *n*-alkyllithium compounds in mixed solvent systems

The use of tetrahydrofuran as a solvent for organolithium reagents is known to enhance the reactivity of these compounds in metalation¹⁻³ and in displacement reactions⁴. Organolithium compounds can be prepared in tetrahydrofuran alone at low temperatures⁵; however, *n*-alkyllithium compounds have been found to be unstable in tetrahydrofuran at room temperature. *n*-Butyllithium under these conditions decomposes completely within two hours, as indicated by the color test for organometallic compounds⁴. In general, the organolithium compounds used in these studies were prepared in diethyl ether, and the subsequent reaction carried out in tetrahydrofuran. This procedure resulted in a mixed solvent system of diethyl ether and tetrahydrofuran.

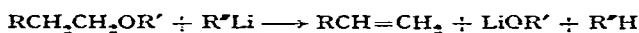
The rates of decomposition of benzyl-, methyl-, α -methylbenzyl-, and phenyllithium have been studied in a quantitative manner⁵ and these compounds have been found to decompose more rapidly in the order given. It is apparent that *n*-alkyllithium compounds, which are more generally used for metalating and halogen-metal interconversion agents, are less stable⁴ than the reagents mentioned above, however, no quantitative study has been carried out. The problem of stability is important with respect to the efficiency of metalation or displacement reactions in solvents where decomposition of the reagent may be rapid.

The stability of some model compounds in mixtures of tetrahydrofuran and diethyl ether (about 1:1 by volume) was investigated. For purposes of comparison, mixtures of diethyl ether with tetrahydropyran and diethyl ether with 2,2,4,4-tetra-

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methyltetrahydrofuran were also investigated. Utilizing the semiquantitative method of the color test, it was found that *n*-butyllithium was completely decomposed in ether-tetrahydrofuran within twenty-four hours at the reflux temperature. Negative color tests were obtained for *n*-butyllithium in ether-tetrahydropyran and ether-2,2,4,4-tetramethyltetrahydrofuran under the same conditions after one week and three weeks, respectively. Tetrahydrofuran therefore enhances the decomposition of *n*-butyllithium to a very marked degree.

When *n*-tetradecyllithium and *n*-decyllithium were refluxed in ether-tetrahydrofuran for forty-eight hours to give a negative color test, the major products isolated in each case were *n*-tetradecane and *n*-decane, respectively, indicating that the major course of decomposition was one involving a metalation reaction. Organolithium compounds react with common alkyl ethers having β -hydrogen atoms to give an olefin product along with an alkoxide⁷ according to the general reaction.



An attempt was made to form derivatives with partly decomposed *n*-decyllithium in ether-tetrahydropyran and in ether-2,2,4,4-tetramethyltetrahydrofuran with chlorotriphenylsilane. There was isolated impure *n*-decyltriphenylsilane which could not be purified by fractional crystallization techniques. This might indicate that organolithium compounds other than *n*-decyllithium had in some manner formed in the solution. In the case of the decomposition of *n*-butyllithium in ether-tetrahydrofuran, ethanol was isolated in high yield. Therefore, the pathway of decomposition in these solvent systems is most probably not an extraordinary one.

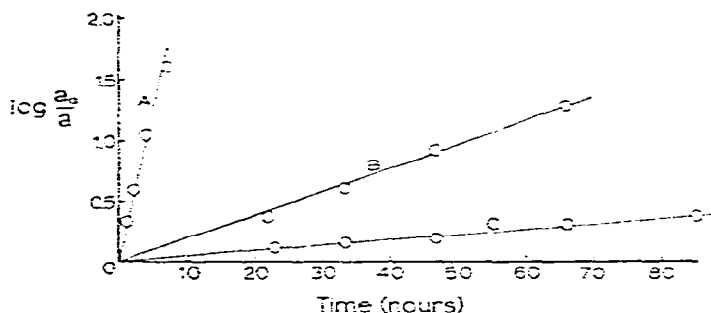


Fig. 1. $\log (a_0/a)$ vs. time for *n*-decyllithium at room temperature in diethyl ether-tetrahydrofuran (A), diethyl ether-tetrahydropyran (B), and diethyl ether-2,2,4,4-tetramethyltetrahydrofuran (C).

TABLE I

STABILITY OF *n*-DECYLLITHIUM IN MIXED SOLVENT SYSTEMS AT ROOM TEMPERATURE

Solvent	k_1 (h^{-1})	$t_{0.5}$ (h)
Diethyl ether-tetrahydrofuran	0.595	1.2
Diethyl ether-tetrahydropyran	0.0450	15
Diethyl ether-2,2,4,4-tetramethyltetrahydrofuran	0.0104	67
Diethyl ether	0.0096	72

A kinetic study concerning the decomposition of *n*-decyllithium in the three mixed solvent systems as well as in diethyl ether was carried out. The stability of *n*-decyllithium in each of the solvents was determined by titrating each reaction mixture periodically, employing the method of double titration using benzyl chloride* (Ref. 8). The kinetic data obtained from these experiments are graphically represented in Fig. 1 and are summarized in Table 1.

The decomposition of *n*-decyllithium in each of the solvents is first order in organolithium compound concentration over at least 80% of the reaction, with the decomposition being sixty times faster in diethyl ether-tetrahydrofuran than in diethyl ether alone. It will be noted that in the presence of tetrahydrofuran the decomposition is very rapid and that when metalations are being carried out in this system under these conditions, consideration must be given to the rate of decomposition of the alkylolithium compounds.

Experimental

Preparation of n-butyllithium in diethyl ether. *n*-Butyllithium was prepared from *n*-butyl bromide and lithium in diethyl ether using a previously described procedure¹⁰.

Preparation of n-decylithium and n-tetradecyllithium in diethyl ether. These two long chain alkylolithium compounds were prepared in a similar manner. In a typical procedure, 10 ml of a solution of 250.0 g (1.13 moles) of *n*-decyl bromide dissolved in 850 ml of diethyl ether was added to 18.8 g (2.71 g-atoms) of lithium metal suspended in 100 ml of diethyl ether. After stirring for 15 min at room temperature, the mixture became cloudy and Color Test I⁶ was positive. The stirred reaction mixture was cooled by means of a Dry Ice-acetone bath to -10° and the remainder of the *n*-decyl bromide solution was added dropwise over a period of 5 h with the temperature being maintained at $-10 \pm 5^{\circ}$. The resulting solution was stirred for an additional 2 h at 0° , and then was transferred to a graduated addition funnel with filtration through glass wool to remove the excess lithium. The yield of *n*-decyllithium, determined by the method of double titration (benzyl chloride)⁸, was 0.922 mole (81.5%) in 1071 ml of solution.

Relative stabilities of n-butyllithium in ether-tetrahydrofuran, ether-tetrahydropyran, and ether-2,2,4,4-tetramethyltetrahydrofuran. A solution of *n*-butyllithium in diethyl ether (100 ml, 0.972 M) was added each to 100 ml of tetrahydrofuran, tetrahydropyran, and 2,2,4,4-tetramethyltetrahydrofuran^{**}. Each mixture was refluxed and required 24 h, one week, and 3 weeks, respectively, to give a negative Color Test I⁶.

Decomposition of n-butyllithium in ether-tetrahydrofuran. To 90 ml of tetrahydrofuran was added 100 ml of a 0.810 M solution of *n*-butyllithium in diethyl ether. After stirring the mixture for 24 h at room temperature, Color Test I⁶ was negative. The reaction mixture was hydrolyzed, and the aqueous layer saturated with sodium chloride and extracted with ether. After drying, the organic layers were distilled to give 3.60 g (96%) of ethyl alcohol, b.p. $75-77^{\circ}$. n_D^{20} 1.3640, identified by means of its 3,5-dinitrobenzoate, m.p. $92-93.5^{\circ}$ (mixed m.p.).

Decomposition of n-tetradecyllithium in ether-tetrahydrofuran. To 65 ml of tetrahydrofuran was added 198 ml of a 0.691 M solution of *n*-tetradecyllithium in diethyl

* For a discussion of the double titration procedure using various organic halides see ref. 9.

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ether. After stirring for 16 h at room temperature and 24 h at reflux, Color Test I⁶ was negative. Hydrolysis with a saturated ammonium chloride solution followed by extraction with ether and then removal of the solvents gave a pale yellow oil, which was distilled under reduced pressure. At 10 mm, 15.83 g (58%) of crude tetradecane, n_D^{20} 1.4302, boiling over the range 120–148°, was obtained. A redistillation did not effect appreciable further purification [13.9 g (51%), n_D^{20} 1.4302, b.p. 115–117/10 mm]. Chromatography of the distillation residue afforded 0.65 g of octacosane m.p. 60–61.5° (mixed m.p.) and a small amount of tetradecanol, m.p. 37–38°.

*Decomposition of *n*-decyllithium in ether-tetrahydrofuran.* A solution of *n*-decyllithium solution in diethyl ether (178 ml, 0.647 M) was added to 65 ml of tetrahydrofuran. A negative Color Test I⁶ was obtained after 48 h of refluxing of the stirred mixture. Hydrolysis followed by the usual extractive procedure led to an oil which was distilled through a packed column to give 12.79 g (78.2%) of *n*-decane, b.p. 170–171.8° n_D^{20} 1.4119. Fractional distillation at reduced pressure of the residue resulted in 0.92 g (5.8%) of less pure *n*-decane, b.p. 59–62°/11 mm, n_D^{20} 1.4128.

*Relative stability of *n*-decyllithium in mixed solvents.* A solution of *n*-decyllithium in diethyl ether (265 ml, 0.860 M) was added each to 225 ml of tetrahydropyran, and 2,2,4,4-tetramethyltetrahydrofuran, and 139 ml of a 1.08 M solution of *n*-decyllithium in diethyl ether to 139 ml of tetrahydrofuran. The mixtures were stirred at room temperature and periodically aliquots were taken to determine the total base and alkylolithium content of each mixture. The data obtained are summarized in Table I and are graphically represented in Fig. 1.

*Stability of *n*-decyllithium in diethyl ether.* To 129 ml of diethyl ether was added 100 ml of a 1.06 M *n*-decyllithium solution in diethyl ether. The reaction mixture was stirred at room temperature and titrated periodically. After 72 h a heavy white precipitate formed and persisted until after Color Test I⁶ was negative (3½ weeks). The precipitate appeared to be a complex containing the alkylolithium compound because during the latter stages of the reaction Color Test I⁶ was positive for the precipitate but negative for the supernatant liquid.

*Derivatization of *n*-decyllithium in ether-tetrahydropyran.* At 22 h a 50 ml aliquot (0.00985 mole of RLi) of the solution of *n*-decyllithium solution in ether-tetrahydropyran solution used above in the stability study was removed and added to 2.91 g (0.00985 mole) of triphenylchlorosilane dissolved in 50 ml of diethyl ether cooled to ice-bath temperature. After 7 h Color Test I⁶ was negative. The usual work-up followed by chromatography on an alumina column resulted in 2.05 g (52%) of crude *n*-decyltriphenylsilane, m.p. 46–55°. The infrared spectrum of this material was the same as a spectrum of authentic *n*-decyltriphenylsilane, however, attempts to purify it were unsuccessful.

*Derivatization of *n*-decyllithium in ether-2,2,4,4-tetramethyltetrahydrofuran.* After 66 h a 50 ml aliquot (0.00995 mole) of the reaction mixture of *n*-decyllithium with ether-2,2,4,4-tetramethyltetrahydrofuran was treated with an equivalent amount of triphenylchlorosilane dissolved in 50 ml of ether. The mixture was stirred at room temperature for 24 h and then worked up in a manner similar to the previous reaction. Again a crude *n*-decyltriphenylsilane (3.0 g, 75%) melting over the range 40–60° was obtained and could not be purified by rechromatography, recrystallization, or sublimation. The infrared spectrum of this material and that of *n*-decyltriphenylsilane were superimposable.

Preparation of n-decyltriphenylsilane. A solution of 0.086 mole of *n*-decyllithium in 100 ml of diethyl ether was added to 25.35 g (0.086 mole) of chlorotriphenylsilane dissolved in 100 ml of ether at ice-bath temperature. After seven h of stirring at room temperature, Color Test I⁶ was negative. After hydrolysis with water the reaction mixture was worked up in the usual manner. A portion of the product was lost mechanically during work-up. However, 8.72 g (25.3%) of crude *n*-decyltriphenylsilane, m.p. 64–69°, was obtained. One recrystallization from ethanol afforded pure product, m.p. 68–69.5° (mixed m.p.).

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Isolation of a compound containing the trimethyltin cation dihydrate

In 1960 Okawara *et al.*¹ suggested, on the basis of the infrared spectra of trimethyltin fluoride and carboxylates, the existence of the planar trimethyltin cation, $(\text{CH}_3)_3\text{Sn}^+$, in the solid state. Although their interpretation was soon questioned by Beattie², the interest of many organotin chemists has been, since then, focused on the unique structural properties of organotin derivatives. Several following investigations^{3–5} have shown the polymeric structure for these compounds by the bridging of the anionic group, F or OOCR, to the trialkyltin group, resulting a pentacoordinated structure for the tin atom. Among similar investigations^{6–13}, Clark¹³ showed that trimethyltin perchlorate and nitrate form diammonia adducts, which on the basis of their infrared spectra were indicated to be ionic compounds formulated as $[(\text{CH}_3)_3\text{Sn}(\text{NH}_3)_2]^+\text{X}^-$, the tin atom still having a trigonal bipyramidal configuration.

In this present investigation we have isolated for the first time a compound containing the dihydrated trimethyltin cation. This novel compound was obtained by reaction of trimethyltin chloride and sodiumtetraphenylborate in water. The infrared spectrum of $[(\text{CH}_3)_3\text{Sn}(\text{OH}_2)_2]^+[\text{B}(\text{C}_6\text{H}_5)_4]^-$ shows only one band in the 500–580 cm^{-1} region, indicating a planar $(\text{CH}_3)_3\text{Sn}$ arrangement¹. The rest of the spectrum is

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