highest experimentally accessible THF/n-C_4H_9Li ratio of 25. In 100% THF the rate is essentially instantaneous. Assuming that reaction (1) does not have a rate maximum at a higher THF/n-C_4H_9Li ratio, the decrease in rate with added n-butyllithium can be interpreted as indicating the existence of a least two etherates of n-butyllithium, and that the higher etherate is more reactive than the lower etherate. If such is the case, the relative reactivities required of the respective etherates are opposite to those invoked to explain a rate maximum. If reaction (1) does have a rate maximum at THF/n-C_4H_9Li > 25, the decrease in rate on adding n-butyllithium at constant THF level can only be explained by the existence of a relatively unreactive solvated n-C_4H_9Li cluster[14].

It is apparent from the trends reported here and the behavior of other organolithium systems that the findings for one reaction or a specific organolithium compound should not be extrapolated to other systems. Presumably with the availability of more data, generalities will be forthcoming. This work is continuing and will be reported in detail soon.

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Received January 15th, 1965

J. Organometal. Chem., 3 (1965) 481–484

The preparation of trialkyltin hydrides by thermal decomposition of formates

Organotin hydrides usually are prepared by the reduction of organotin halides or oxides. We now wish to report that tri-n-propyltin or tri-n-butyltin hydride can be prepared by thermal decomposition of the corresponding formate under vacuum:

$$R_3SnOOCH \xrightarrow{\Delta} R_3SnH + CO_2$$

Tri-n-propyltin formate[1] (27.7 g, b.p. 101–104°/3 mm Hg, n_D^{20} 1.5038) was heated at 160–170° under reduced pressure (10–12 mm Hg), using a distillating column

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packed with glass Raschig rings to separate the hydride from the starting material during the course of reaction. After about 8 h, 5.6 g of tri-*n*-propyltin hydride was obtained (about 25 % conversion). In the case of tri-*n*-butyltin formate, undistilled material (35.2 g), which was obtained by dissolving bis(tri-*n*-butyl)tin oxide into a slight excess of formic acid, was treated as above at 170–180° under 1 mm Hg for 9 h, and tri-*n*-butyltin hydride (18.4 g) was obtained (about 60 % conversion). In both cases the unreacted starting materials were confirmed by their infrared spectra to be almost unchanged $R_3SnOOCH$. These hydrides $(n\text{-}C_3H_7)_3SnH$ (Found: C, 43.17; H, 8.93. $C_9H_{22}Sn$ calcd.: C, 43.42, H, 8.91 %.) and $(n\text{-}C_4H_9)_3SnH$ (Found: C, 49.85; H, 9.88. $C_{12}H_{28}Sn$ calcd.: C, 49.52; H, 9.70 %.) had the strong infrared absorption near 1800 cm^{-1} characteristic of tin hydrides. Furthermore, their infrared spectra in the NaCl and KBr region were identical with those of authentic samples prepared by the reduction of halides with $LiAlH_4$.

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Received March 3rd, 1965

J. Organometal. Chem., 3 (1965) 484–485

Infrarot-Spektren von Organometall-Schwefel-, -Selen- und -Tellur-Verbindungen

Von den Metallorganischen Verbindungen der schweren IVb-Elemente wurden vor allem die Infrarot- und Ramanspektren der Zinnorganyle bisher eingehend untersucht[1–12]. Neben der Zuordnung der Schwingungsspektren von Zinntetraorganylen, Organozinnhalogeniden, -oxiden und -hydriden wurden auch die IR- und Ramanfrequenzen einiger Alkylzinnsulfide und -selenide[10] im Bereich bis 400 cm^{-1} mitgeteilt.

Im Anschluss an präparative Arbeiten[13–16] haben wir die Infrarot-Spektren von Verbindungen der allgemeinen Formel $(C_6H_5)_3M\text{–}X\text{–}M'(C_6H_5)_3$ [M und M' = Ge, Sn, Pb; X = S, Se, Te] im Bereich zwischen 250 und 5000 cm^{-1} untersucht*. Wir erhielten die Verbindungen durch doppelte Umsetzungen aus den Lithium-triphenylmetallchalkogeniden mit Triphenylbromgerman, Triphenylchlorstannan oder Triphenylchlorplumban

$$(C_6H_5)_3M\text{–}X\text{–}Li + ClM'(C_6H_5)_3 \longrightarrow LiCl + (C_6H_5)_3M\text{–}X\text{–}M'(C_6H_5)_3 \qquad (1)$$

Nach Aussonderung der bis auf wenige Ausnahmen nahezu lagekonstanten inneren Schwingungen der Phenylkerne[17] bleiben die in Tabelle 1 und 2 aufgeführten Banden, die den Gerüstschwingungen dieser Moleküle zuzuordnen sind. In den bei

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* Perkin-Elmer, Modell 221, NaCl und CsBr-Prismen, in Nujol-suspension zwischen entspr. Fenstermaterial.

J. Organometal. Chem., 3 (1965) 485–487