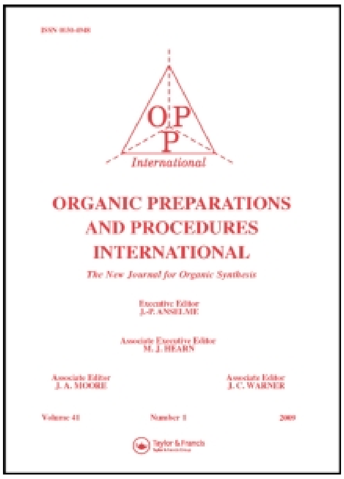

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MONO- AND DIKETONES FROM ALKYLTIN CARBOXYLATES

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7. All melting points are uncorrected. Refractive indices were determined on a Bausch and Lomb Abbe Refractometer. IR spectra were run on a Perkin-Elmer 257 Spectrophotometer. Nmr spectra were obtained at 60 M Hz on a Hitachi Perkin-Elmer R-20 Spectrometer. The solvent used was d-chloroform (1% TMS as internal standard). The chemical shifts are given in δ-values, in parts per million downfield from TMS.

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MONO- AND DIKETONES FROM ALKYLTIN CARBOXYLATES

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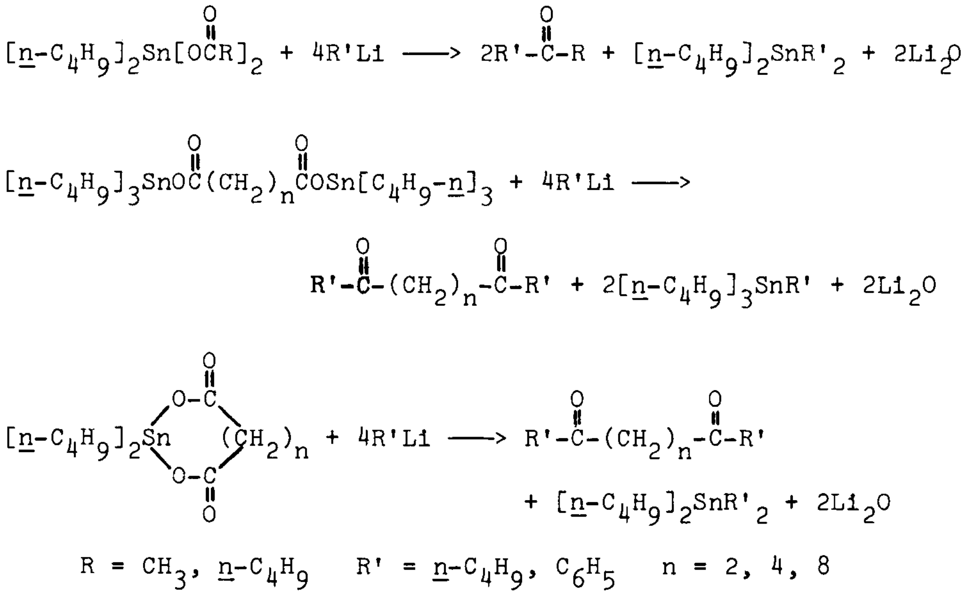

$$[\underline{n}\text{-}C_4H_9]_2Sn[O\overset{O}{\overset{\|}{C}}R]_2 + 4R'Li \longrightarrow 2R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}R + [\underline{n}\text{-}C_4H_9]_2SnR'_2 + 2Li_2O$$

$$[\underline{n}\text{-}C_4H_9]_3SnO\overset{O}{\overset{\|}{C}}(CH_2)_n\overset{O}{\overset{\|}{C}}OSn[C_4H_9\text{-}\underline{n}]_3 + 4R'Li \longrightarrow R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_n\text{-}\overset{O}{\overset{\|}{C}}\text{-}R' + 2[\underline{n}\text{-}C_4H_9]_3SnR' + 2Li_2O$$

$$+ 4R'Li \longrightarrow R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_n\text{-}\overset{O}{\overset{\|}{C}}\text{-}R' + [\underline{n}\text{-}C_4H_9]_2SnR'_2 + 2Li_2O$$

$R = CH_3, \underline{n}\text{-}C_4H_9 \quad R' = \underline{n}\text{-}C_4H_9, C_6H_5 \quad n = 2, 4, 8$

In an extension of previous work[1] it is found that mono- and diketones are obtained from organotin esters[2,3] by reaction with alkyl or aryl lithium compounds. Aliphatic dicarboxylic esters have been reported to react with lithium reagents to give bitertiary glycols;[4] lithium carboxylates, carboxylic acids and esters have produced ketones and tertiary alcohols by reaction with organolithium compounds.[6,7] Studies of the kinetics and mechanism of some of these reactions have been reported.[5,6,8]

Di-n-butyltin sebacate had been reported[3] to be a straight chain heptamer; however, recrystallization from xylene/n-hexane at -20°C gave a product (mp. 80-82°C) which exhibited no free acid group in the infrared spectrum indicating a cyclic structure. The gaseous cyclic product is monomeric as determined by mass spectroscopy. Cyclic di-n-butyltin esters of adipic and succinic acids[3] are trimeric in the vapor state.

EXPERIMENTAL

5,8-Dodecanedione: At 0°C (internal temperature, ice-salt bath) an ethereal solution of n-butyllithium (5.12 g in 55 ml) was added dropwise with stirring to a suspension of bis(tri-n-butyltin)succinate (13.9 g) in 200 ml of anhydrous ether under an argon atmosphere. After addition the reaction mixture was stirred at 0°C for three hours and then hydrolyzed at 0°C with 150 ml of 5% potassium chloride solution. After extraction with three 150 ml portions of ether the combined extracts were washed with water, dried over anhydrous sodium sulfate, filtered and concentrated (16.7 g).

Chromatography on neutral alumina (petroleum ether, bp. 30-60°C) afforded 13.2 g of tetra-n-butyltin as the first fraction, identical with an authentic sample by comparison of IR, VPC and refractive index. Elution with benzene gave 0.72 g of the diketone, mp. 48-50°C which after recrystallization from petroleum ether (charcoal) melted at 49.5-50.5°C.

An nmr spectrum of the diketone, in carbon tetrachloride, was determined on the Varian A-60, Analytical nmr Spectrometer. The ratio of methylene protons adjacent to the carbonyl groups (7.70 τ) to nonadjacent protons (8.70 τ) was found to be 8.17:13.9) This is consistent with the 5,8 position of the carbonyl groups.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18; Mol.wt., 198.
Found: C, 72.93; H, 10.90; Mol.wt., 194 (benzene).

Acetophenone: Phenyllithium reagent (6.7 g in 38 ml of 30:70 ether:benzene with 15% mineral oil) was reacted as above with di-*n*-butyltin acetate (7.01 g) except that the internal temperature was -70°C (acetone, dry-ice bath). After three hours, the temperature was allowed to rise to 0°C, the mixture was hydrolyzed and processed as above. The first chromatographic fraction (eluted with petroleum ether) was a mixture of mineral oil and di-*n*-butyldiphenyltin which was distilled to give pure product: 6.42 g; bp. 137°/0.2 mm. Elution with benzene isolated 0.82 g of acetophenone; these products were characterized as above.

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The findings in this report are not to be construed as an official position of the Department of the Army.

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CORRECTION

Vol. 1, p. 329 (1969). Under Cleaning Solution should read:

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