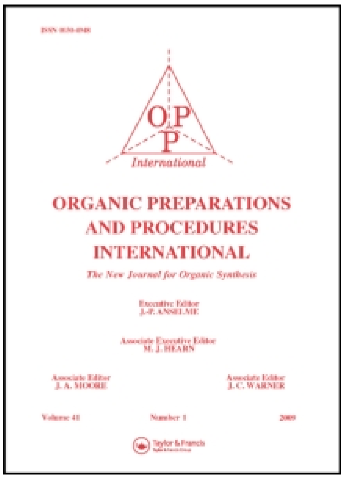

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ANHYDRIDE FORMATION WITH THIONYL CHLORIDE

Jerry M. Adduci[a]; Rene S. Ramirez[a]
[a] Department of Chemistry, Rochester Institute of Technology, Rochester, New York

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OPP REPORTS

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ANHYDRIDE FORMATION WITH THIONYL CHLORIDE

Submitted by Jerry M. Adduci and Rene S. Ramirez[1]

Department of Chemistry
Rochester Institute of Technology
Rochester, New York 14623

$$2RCOOH + SOCl_2 \longrightarrow (RCO)_2O + SO_2 + HCl$$

The reaction of a monocarboxylic acid with thionyl chloride in a 2 to 1 mole ratio appears to be a general method for preparing symmetrical acid anhydrides. Table I summarizes yields of anhydrides prepared by this method.

It has been reported that monocarboxylic acids and thionyl chloride yield anhydrides only in the presence of pyridine.[2,3] Thionyl chloride has been used as a dehydrating agent for the preparation of anhydrides of di-, tri- and tetracarboxylic acids[4-6] and their silver salts[2] to form 5- and 6-membered rings.

Table I.

Alkyltin Carboxylates	Reagent	Solvent	Temp °C	Ref	Ketone	Yield %	R_4Sn	Yield %
$[n\text{-}C_4H_9]_2Sn[OCOCH_3]_2$	$n\text{-}C_4H_9Li$	Et_2O	-70	10	$n\text{-}C_4H_9\overset{\overset{O}{\|}}{C}CH_3$	40	$[n\text{-}C_4H_9]_4Sn$	80
	C_6H_5Li	THF	-70	11	$C_6H_5\underset{\underset{O}{\|}}{C}CH_3$	34	$[n\text{-}C_4H_9]_2[C_6H_5]_2Sn$	83
$[n\text{-}C_4H_9]_2Sn[OCO(CH_2)_{10}CH_3]_2$	$n\text{-}C_4H_9Li$	THF	-70	12	$n\text{-}C_4H_9\overset{\overset{O}{\|}}{C}(CH_2)_{10}CH_3$	45	$[n\text{-}C_4H_9]_4Sn$	99
	C_6H_5Li	THF	-70	13	$C_6H_5\underset{\underset{O}{\|}}{C}(CH_2)_{10}CH_3$	41	$[n\text{-}C_4H_9]_2[C_6H_5]_2Sn$	85
$[n\text{-}C_4H_9]_3SnOCO(CH_2)_2OCOSn[C_4H_9\text{-}n]_3$	$n\text{-}C_4H_9Li$	Et_2O	0		$n\text{-}C_4H_9\overset{\overset{O}{\|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C}C_4H_9\text{-}n$	18	$[n\text{-}C_4H_9]_4Sn$	95
	C_6H_5Li	Et_2O	0	14	$C_6H_5\underset{\underset{O}{\|}}{C}(CH_2)_2\underset{\underset{O}{\|}}{C}C_6H_5$	18	$[n\text{-}C_4H_9]_3C_6H_5Sn$	99
$[n\text{-}C_4H_9]_3SnOCO(CH_2)_4OCOSn[C_4H_9\text{-}n]_3$	$n\text{-}C_4H_9Li$	Et_2/THF 1:1	-70	15	$n\text{-}C_4H_9\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}C_4H_9\text{-}n$	27	$[n\text{-}C_4H_9]_4Sn$	90
$[n\text{-}C_4H_9]_3SnOCO(CH_2)_8OCOSn[C_4H_9\text{-}n]_3$	$n\text{-}C_4H_9Li$	Et_2O	25	16	$n\text{-}C_4H_9\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}C_4H_9\text{-}n$	21	$[n\text{-}C_4H_9]_4Sn$	89
	$n\text{-}C_4H_9Li$	THF	25	16	$n\text{-}C_4H_9\underset{\underset{O}{\|}}{C}(CH_2)_8\underset{\underset{O}{\|}}{C}C_4H_9\text{-}n$	36	$[n\text{-}C_4H_9]_4Sn$	95
	C_6H_5Li	THF	-70	17	$C_6H_5\underset{\underset{O}{\|}}{C}(CH_2)_8\underset{\underset{O}{\|}}{C}C_6H_5$	24	$[n\text{-}C_4H_9]_3C_6H_5Sn$	72
$[n\text{-}C_4H_9]_2\underbrace{SnOCO(CH_2)_2OCO}$	$n\text{-}C_4H_9Li$	Et_2O	0		$n\text{-}C_4H_9\overset{\overset{O}{\|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C}C_4H_9\text{-}n$	20	$[n\text{-}C_4H_9]_4Sn$	65
	C_6H_5Li	THF	-70	14	$C_6H_5\underset{\underset{O}{\|}}{C}(CH_2)_2\underset{\underset{O}{\|}}{C}C_6H_5$	10	$[n\text{-}C_4H_9]_2[C_6H_5]_2Sn$	85
$[n\text{-}C_4H_9]_2\underbrace{SnOCO(CH_2)_4OCO}$	$n\text{-}C_4H_9Li$	Et_2O	-70	15	$n\text{-}C_4H_9\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}C_4H_9\text{-}n$	16	$[n\text{-}C_4H_9]_4Sn$	50
	$n\text{-}C_4H_9Li$	THF	-70	15	$n\text{-}C_4H_9\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}C_4H_9\text{-}n$	11	$[n\text{-}C_4H_9]_4Sn$	98
$[n\text{-}C_4H_9]_2\underbrace{SnOCO(CH_2)_8OCO}$	$n\text{-}C_4H_9Li$	THF	25	16	$n\text{-}C_4H_9\overset{\overset{O}{\|}}{C}(CH_2)_8\overset{\overset{O}{\|}}{C}C_4H_9\text{-}n$	28	$[n\text{-}C_4H_9]_4Sn$	98
	$n\text{-}C_6H_5Li$	THF	25	17	$C_6H_5\underset{\underset{O}{\|}}{C}(CH_2)_8\underset{\underset{O}{\|}}{C}C_6H_5$	18	$[n\text{-}C_4H_9]_2[C_6H_5]_2Sn$	98

All reactions were three hours.

Hydrolysis temperature, 0°C.

The ketones and tin compounds were isolated chromatographically.

Elution with petroleum ether resulted in $R_3C_6H_5Sn$ and $R_2(C_6H_5)_2Sn$ mineral oil mixtures. The tin compounds were then purified by distillation.

SYNTHESIS OF ACID ANHYDRIDES

STARTING MATERIALS[a]		PRODUCTS		
Acid (mole)	Benzene ml.	mp.,bp. °	n_D^{20}	Yield %
Acetic (0.4)	--	138	1.3884	81[b]
Propionic (0.2)	--	166	1.4038	80[b]
Diphenylacetic (0.1)	25	96	--	78[g]
Bromoacetic (0.1)	35	40	--	76[c]
Trimethylacetic (0.2)	40	188	1.4092	71[c]
Palmitic (0.05)	60	61-62	--	87[f]
Benzoic (0.05)	30	40-44	--	57[d]
Chloroacetic (0.2)	30	38-40	--	--[e]

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a) In all runs, a 2:1 ratio of acid:thionyl chloride was used; reflux time was 60 hrs. except as otherwise noted.

b) Anhydride purified by fractional distillation.

c) Anhydride purified by vacuum distillation.

d) Reflux time was 20 hrs., from pet ether.

e) Yield could not be determined. The anhydride could not be separated completely from the starting acid; from 7:3 pet ether:chloroform.

f) From pet ether.

g) From 9:1 pet ether:benzene.

EXPERIMENTAL[7]

Typical procedures for a liquid and a solid anhydride are described below.

Acetic Anhydride. Acetic acid (24 g., 0.4 mole) was refluxed with thionyl chloride (23.8 g., 0.2 mole) for 20 hrs. Fractional distillation yielded 16.6 g. (81%) of acetic anhydride, bp. 138°, n_D^{20} 1.3884 (lit.[8] bp. 138°, n_D^{20} 1.3901). Acetic acid (3.4 g.) was recovered. The IR spectrum was identical to that of a known sample of acetic anhydride.[9] The nmr spectrum showed a single signal at 2.15 ppm.

Diphenylacetic Anhydride. Diphenylacetic acid (21.2 g., 0.1 mole) in 25 ml. of benzene was refluxed with thionyl chloride (5.9 g., 0.05 mole) for 20 hrs. The benzene was removed under vacuum and the crude anhydride (19.9 g.) was recrystallized from a petroleum ether-benzene (9:1) mixture giving 15.9 g. (78%) of diphenylacetic anhydride, mp. 96° (lit.[8] mp. 98°). The IR spectrum showed strong absorptions at 1810 and 1740 cm^{-1} indicative of an anhydride group. The nmr spectrum exhibited aromatic absorptions centered at 7.18 ppm (10 H) and a singlet at 4.95 ppm (1 H). The spectrum was consistent with the structure of diphenylacetic anhydride.

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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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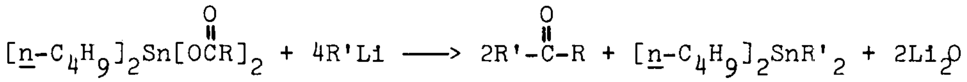
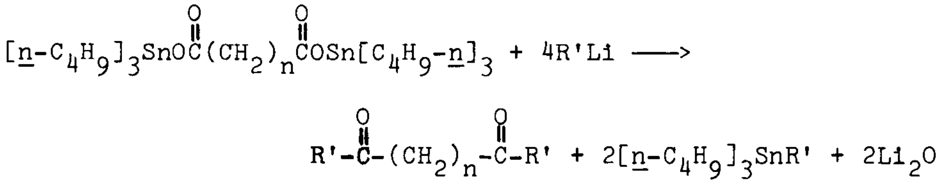
MONO- AND DIKETONES FROM ALKYLTIN CARBOXYLATES

Submitted by Bernard R. LaLiberte, Helmut F. Reiff
and Wenzel E. Davidsohn

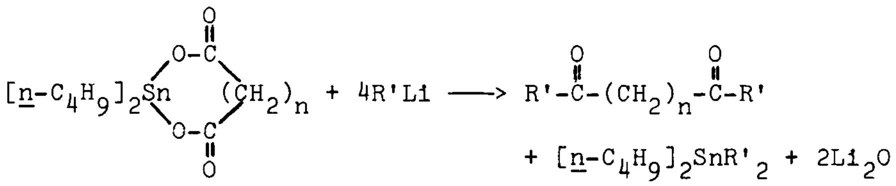
Army Materials and Mechanics
Research Center
Watertown, Massachusetts 02172



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



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



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