(d, 1 H, J = 7.8 Hz), 8.35 (s, 1 H), 8.40 (d, 1 H, J = 8.0 Hz). IR: 3363, 1605, 1590, 1574, 1556, 1532 cm^{-1}. Anal. Calcd for $C_{13}H_{10}ClNOTe$: C, 43.46; H, 2.81. Found: C, 43.50; H, 2.77.

2-[(Phenylamino)carbonyl]benzenetellurenyl bromide (7b) was similarly prepared by treatment of dianion **6c** with $CuBr_2$ (2 equiv; 43% yield of **7b**) or Br_2 (1 equiv; 66% yield of **7b**); mp 198 °C. The material seemed to partly decompose during recrystallization, and no satisfactory elemental analysis was obtained. ^1H NMR: δ 7.31 (m, 1 H), 7.41–7.70 (several peaks, 6 H), 7.85 (d, 1 H, J = 7.7 Hz), 8.31 (s, 1 H), 8.43 (d, 1 H, J = 7.9 Hz). IR: 3366, 1605, 1590, 1573, 1554, 1532 cm^{-1}. Treatment of the material in CH_2Cl_2 with 1 equiv of bromine, followed by precipitation with hexane, caused separation of 2-[(phenylamino)carbonyl]-benzenetellurium tribromide. Anal. Calcd for $C_{13}H_{10}Br_3NOTe$: C, 27.71; H, 1.79. Found: C, 27.96; H, 1.78.

2-[(Phenylamino)carbonyl]benzenetellurenyl iodide (7c) was similarly prepared by treatment of dianion **6c** with I_2 (1 equiv) in 72% yield, mp 170–1 °C. ^1H NMR: δ 7.28 (m, 1 H), 7.42–7.62 (several peaks, 6 H), 7.75 (d, 1 H, J = 7.4 Hz), 8.24 (s, 1 H), 8.38, (d, 1 H, J = 7.7 Hz). IR: 3384, 1602, 1588, 1573, 1543 cm^{-1}. Anal. Calcd for $C_{13}H_{10}INOTe$: C, 34.64; H, 2.24. Found: C, 34.76; H, 2.27.

2,2'-Diselenobis(benzanilide) (8). When a solution of dianion **6b** (prepared as described for compound **4b**) was poured into a solution of $K_3Fe(CN)_6$ (1.70 g, 5.2 mmol) in water (100 mL), 1.10 g (79%) of compound **8** separated out as a yellowish solid, mp 256–7 °C (1,2-dichlorobenzene) (lit.[11] mp 263–5 °C). ^1H NMR (DMSO-d_6): δ 7.16 (m, 1 H), 7.38–7.47 (several peaks, 4 H), 7.77–7.81 (several peaks, 3 H), 7.96 (d, 1 H, J = 6.7 Hz), 10.6 (s, 1 H). IR: 3293 and 1639 cm^{-1}. Anal. Calcd for $C_{13}H_{10}NOSe$: C, 56.74; H, 3.66. Found: C, 56.65; H, 3.64.

Acknowledgment. Financial support by the National Swedish Board for Technical Development and the Swedish Natural Science Research Council is gratefully acknowledged.

Registry No. **1a**, 2527-03-9; **1b**, 60940-34-3; **4a**, 22978-26-3; **4b**, 60940-24-1; **4c**, 119796-32-6; **6a**, 119796-33-7; **7a**, 119796-34-8; **7b**, 119796-36-0; **7c**, 119796-35-9; **8**, 106663-84-7; benzanilide, 93-98-1; selenium, 7782-49-2; sulfur, 7704-34-9; tellurium, 13494-80-9.

A General Access to Acylstannanes

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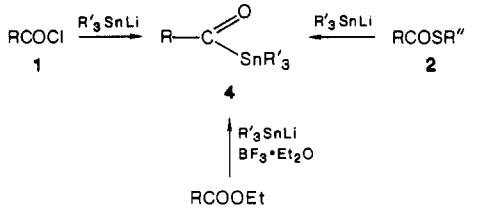
Much recent attention on acylmetallic compounds of group 14 elements has been focused upon their silicon derivatives, interesting both from the synthetic and the spectroscopic point of view.[1] Acylsilanes, in fact, have been shown to be very versatile organometallic reagents, participating in a number of interesting chemical transformations.[2]

Scheme I



On the contrary, very little is known about the corresponding acyltin derivatives,[3] despite their theoretical and practical interest in synthetic organic chemistry, deriving from the expected[4] greater reactivity of the tin–carbon compared to the silicon–carbon bond.

Our long-standing interest in the field of acylsilanes as "umpolung" reagents for nucleophilic acylation[5] has induced us to extend our attention to this promising and almost unexplored class of organometallic derivatives, in order to evaluate their potential in organic synthesis. Two reports dealing with the first examples of the reactivity of this class of compounds[3c,e] have recently appeared, but a general and efficient method for their preparation is still lacking. Furthermore, the very few methods available at present for the synthesis of acylstannanes are of limited interest due to the unavailability or high cost of the starting materials.[3,6]

We would like to report here the development of a new, simple, and possibly general method for the synthesis of acylstannanes.

Several attempts to obtain these tin derivatives through the usual hydrolytic methods[7] did not yield, for different reasons, the desired compounds. 2-(Trialkylstannyl)-2-phenyl-1,3-dithiane, in fact, when hydrolyzed, following several well-known procedures, led either to no reaction or to complete cleavage of the starting material. On the other hand, the difficulties encountered in the stannylation

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(5) (a) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M.; Seconi, G.; Ricci, A.; Fiorenza, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1201. (b) Ricci, A.; Degl'Innocenti, A.; Chimichi, S.; Fiorenza, M.; Rossini, G.; Bestmann, H. J. *J. Org. Chem.* **1985**, *50*, 130. (c) Ricci, A.; Fiorenza, M.; Degl'Innocenti, A.; Seconi, G.; Dembech, P.; Witzgall, K.; Bestmann, H. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1068. (d) Ricci, A.; Degl'Innocenti, A.; Mordini, A.; Reginato, G.; Colotta, V. *Gazz. Chim. Ital.* **1987**, *117*, 645.

(6) An attempt to extend Quintard's[3b] procedure to the synthesis of aromatic acylstannanes by reacting Me_3SnLi with 2 equiv of benzaldehyde led only to the isolation of ((trimethylstannyl)oxy)benzoin in 48% yield, which is probably formed according to the following reaction:

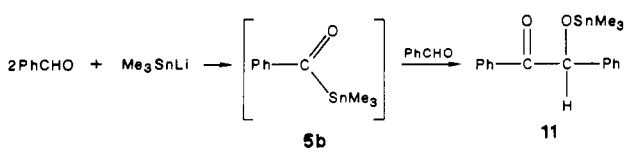

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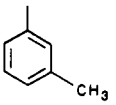
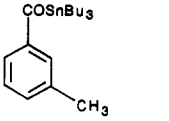
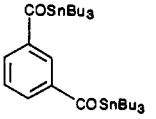
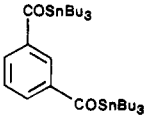
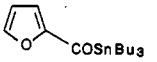
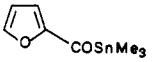
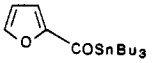
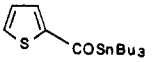
Table I. Synthesis of Acylstannanes through Reaction of RCOX with R'_3SnLi[a]

entry	X	R	R′	Lewis acid	product	yield,[c] %
1	OEt	Ph	*n*-Bu	$BF_3{\cdot}Et_2O$[b]	$PhCOSnBu_3$ **5a**	60
2	SMe	Ph	*n*-Bu		$PhCOSnBu_3$ **5a**	58
3	SMe	Ph	Me		$PhCOSnMe_3$ **5b**	57
4	SPh	Ph	*n*-Bu		$PhCOSnBu_3$ **5a**	62
5	SPh		*n*-Bu		 **6a**	49
6	OMe		*n*-Bu	$BF_3{\cdot}Et_2O$[b]	 **7a**	42[d]
7	SPh		*n*-Bu		 **7b**	48[d]
8	OEt		*n*-Bu	$BF_3{\cdot}Et_2O$[b]	 **8a**	73
9	OEt		Me	$BF_3{\cdot}Et_2O$[b]	 **8b**	15
10	SPh		*n*-Bu		 **8a**	47
11	SPh		*n*-Bu		 **9b**	38
12	SMe	C_3H_7	*n*-Bu		$C_3H_7COSnBu_3$ **10b**	39

[a] All reactions were performed in THF at −78 °C under an inert atmosphere by treating a solution of R'_3SnLi with appropriate electrophile. [b] The optimized molar ratio of carboxylate:R'_3SnLi:$BF_3{\cdot}Et_2O$ 1:2:2.4. [c] Yields determined by quantitative GC/MS analysis. [d] The monoderivative was detected as a byproduct.

of 2-phenyl-1,3-dioxane and dioxolane, and of the *O*-trimethylsilyl and *O*-ethoxyethyl benzaldehyde cyanohydrins, prevented us from exploring the much milder hydrolyses of these protected ketones. All this compelled us to look for a different synthetic approach to this class of compounds, as outlined in Scheme I.

We have found that (trialkylstannyl)lithium reacts with a variety of electrophiles, such as acyl chlorides, ethyl carboxylates, and thioesters, to afford an access to acylstannanes.

Among these three routes the acyl chloride based preparation of acylstannanes turns out to be the less attractive, due to the somewhat lower yields. The reaction mixtures were, in fact, contaminated by sizeable amounts of stannylated byproducts, whose presence, coupled with the lability of acylstannanes toward molecular oxygen, prevented us from obtaining pure samples. In fact, trialkylacylstannanes, contrary to Peddle's findings in the triphenyl series,[3a] are quite reactive toward molecular oxygen, being rapidly degradated upon exposure to air. Neither distillation (Kugelrohr 200 °C, 8×10^{-2} mmHg) nor column chromatography (Florisil, hexane, N_2), allowed us to obtain a pure sample of the target material.[8]

Better results were obtained by reacting Bu_3SnLi and Me_3SnLi with carboxylate esters in the presence of $BF_3{\cdot}Et_2O$[9] or with thioesters, in which case the reactions took place spontaneously. Several ratios of carboxylate esters to $BF_3{\cdot}Et_2O$ and R_3SnLi were used, in the reaction of esters, the best results being obtained with a carboxylate:lithiated tin species:Lewis acid ratio of 1:2:2.4.

Even though the overall yields of the final products obtained through the two above-mentioned procedures are comparable, major advantages of the thioester method lie in the absence of the Lewis acid and especially in the lower amounts of the stannylated byproducts, this reaction being run with equimolar amounts of the two reagents (see the Experimental Section). A further feature of this synthesis is the very easy workup, which is not of secondary importance due to the mentioned lability of these compounds toward molecular oxygen, which precludes long and tedious procedures. Moreover, acylstannanes prepared by this method turn out to be sufficiently pure (ca. 90%) and can

(8) No improvement was obtained even by reacting benzoyl chloride with $R_3SnCu{\cdot}Me_2S$.

(9) Yamaguchi, M.; Shibato, K.; Fujiwara, I. H. *Synthesis* **1986**, 421.

Table II. Spectral Data of Acylstannanes

compd	^{13}C NMR,[a] $\delta_{C=O}$	^{119}Sn NMR,[b] δ	^{29}Si NMR,[a] δ	IR,[c] C=O
5a	244	−84		1615
5b	239.5	−80		1620
8a	230	−84		1600
8b	234	−87		1595
9b	236	−89		1590
10b	249	−90.5		1645
$PhCOSiMe_3$	234.2[d]		−7.9[d]	1617

[a] Spectra recorded in $CDCl_3$ (ppm) with respect to internal Me_4Si. [b] With respect to internal Me_4Sn. [c] In cm^{-1}, as $CDCl_3$ solutions. [d] Dexheimer, E. M.; Buell, G. R.; LeCroix, C. *Spectrosc. Lett.* **1978**, *11*, 751.

be used for subsequent reactions, without further purification.[10]

The relevant results of the above reactions are summarized in Table I. Worth mentioning, in particular, is the possibility of obtaining a general route to the still unreported heteroacylstannanes, which could prove to be, based on their correspondence with the silicon analogues,[5b] even more interesting and synthetically useful than the aromatic or aliphatic derivatives.

All the acylstannanes obtained throughout this work showed, as outlined in Table II, the unusual spectroscopic features previously noticed in the acylsilanes series.[5b,11] The ^{13}C NMR chemical shifts are indicative of an unexpectedly low electron density on the carbonyl carbon, whereas the high upfield shift of the ^{119}Sn suggests abnormally high electron density on the tin atom. The inadequacy of the ketonic structure for the description of the ground-state features of these compounds, already proposed in the case of acylsilanes,[5b] would also seem to apply to the acylstannane series, showing a close relationship between these two classes of acylmetallic derivatives.

Experimental Section

All reactions required dry conditions and were performed in oven-dried (110 °C for more than 2 h) glassware. The reactions as well as the workups, distillation, chromatography, and handling of acylstannanes were performed under a strictly inert atmosphere.

THF was freshly distilled from $LiAlH_4$ prior to use. ^1H, ^{13}C, and ^{119}Sn NMR spectra were obtained on Perkin-Elmer R-32 and Varian VXR-300 spectrometers (operating respectively at 90 and 300 MHz), IR spectra on a Perkin-Elmer 283 spectrophotometer, and GC/MS analysis on an HP5970-HP5790 GC selective ion detector, equipped with a high-performance dimethylsilicone fluid 25-m capillary column.

NMR spectra were recorded as $CDCl_3$ and CCl_4 solutions. Column chromatography was performed on Florisil, under a nitrogen stream.

Bu_3SnLi and Me_3SnLi were prepared according to Still's procedures.[12,13]

Procedure A: Reactions of (Trialkylstannyl)lithium with Esters. (Trialkylstannyl)lithium (0.68 mmol) in 2 mL of THF was treated at −78 °C with the appropriate alkyl carboxylate (0.34 mmol) in 1 mL of THF, followed by addition of $BF_3{\cdot}Et_2O$ (0.8 mmol). The orange solution obtained was stirred for 1 h at −78 °C, diluted with 3 mL of ether, and quenched with saturated NH_4Cl. After reaching room temperature, the aqueous layer was removed and the organic phase was washed with water and brine. Drying over Na_2SO_4 and removal of the solvent afforded the crude acylstannane.

Procedure B: Reactions of (Trialkylstannyl)lithium with Thioesters. (Trialkylstannyl)lithium (0.68 mmol) in 2 mL of THF was treated at −78 °C with an equimolar amount of thioester in 1 mL of THF and stirred for 1 h at −78 °C. Progress of the reactions was monitored by GC/MS analysis, and the reaction mixture was quenched at −78 °C with saturated NH_4Cl and worked up according to the above procedure. Evaporation of the solvent usually led to a thick, orange oil, which was purified by column chromatography (Florisil, hexane, N_2).

Benzoyltrimethylstannane (5b). To a cooled solution (−78 °C) of Me_3SnLi (0.60 mmol) was added dropwise 91.2 mg of PhCOSMe (0.60 mmol, 73 μL) in 1 mL of THF over 3 min. The reaction mixture was stirred for 1 h at −78 °C, diluted with 5 mL of ether, quenched with saturated NH_4Cl, and then slowly warmed to room temperature. The aqueous layer was removed with a syringe, and the organic phase was washed three times with water and brine. The yellow solution obtained was dried over Na_2SO_4, and the solvent was removed under vacuum, giving 250 mg of crude material, which was purified by elution under nitrogen on Florisil with hexane–ether 10:1 as the eluant, yielding 155.7 mg (57.6%) of benzoyltrimethylstannane: IR (CCl_4) 3100–2840, 1620, 1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 7.27–7.35 (m, 3 H), 7.86–8.1 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 239.5 (C=O), 131.8, 129.3, 127.5 ppm; ^{119}Sn NMR ($CDCl_3$) δ −80 ppm; MS *m/e* (relative intensity) 270 (3.1), 165 (56.5), 105 (100), 77 (47.3).

Acknowledgment. Technical assistance from L. Favaretto and A. Guerrini and Financial support by the "Progetto Finalizzato Chimica Fine" CNR, Rome, are gratefully acknowledged.

Registry No. **5a**, 114566-87-9; **5b**, 120086-07-9; **6a**, 120086-08-0; **7a**, 120086-09-1; **8a**, 120086-10-4; **8b**, 120086-11-5; **9b**, 120086-12-6; **10b**, 120086-13-7; PhCOOEt, 93-89-0; PhCOSMe, 5925-68-8; PhCOSPh, 884-09-3; MeC_6H_4-*m*-COSPh, 97839-38-8; $MeOCOC_6H_4$-*m*-COOMe, 1459-93-4; $PhSCOC_6H_4$-*m*-COSPh, 18953-23-6; C_3H_7COSMe, 2432-51-1; $(n\text{-}Bu)_3SnLi$, 4226-01-1; Me_3SnLi, 17946-71-3; 2-furancarboxylic acid ethyl ester, 614-99-3; 2-furancarbothioic acid *S*-phenyl ester, 17357-38-9; 2-thiophenecarbothioic acid *S*-phenyl ester, 28122-95-4; 2-phenyl-1,3-dioxane, 772-01-0; dioxolane, 646-06-0; *O*-trimethylsilyl benzaldehyde cyanohydrin, 25438-37-3; *O*-ethoxyethyl benzaldehyde cyanohydrin, 120086-14-8.

(10) The reactivity of acylstannanes toward several representative electrophiles will be discussed in a forthcoming paper.

(11) (a) Ramsey, B. G.; Brook, A. G.; Bassindale, A. R.; Boch, M. *J. Organomet. Chem.* **1974**, *11*, 751. (b) Dexheimer, E. M.; Buell, G. R.; Le Croix, C. *Spectrosc. Lett.* **1978**, *11*, 751.

(12) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.

(13) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836.

Baeyer–Villiger Oxidation of Hexacyclo[10.2.1.$0^{2,11}$.$0^{4,9}$.$0^{4,14}$.$0^{9,13}$]pentadeca-3,10-dione Systems†

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Baeyer–Villiger (B–V) oxidation of polycyclic ketones has received considerable attention in recent years from synthetic as well as mechanistic considerations.[2] Surapaneni and Gilardi[2a] have reported recently that the B–V oxidation of **2** gave exclusively **3** and not **1** (Scheme I). The structure **3** was unambiguously proved by single-crystal X-ray.

Since B–V oxidations in strained systems involved carbenium ion intermediates which are known to trigger various Wagner–Meerwein type rearrangements, we were interested in knowing whether such possibilities exist in hexacyclo[10.2.1.$0^{2,11}$.$0^{4,9}$.$0^{4,14}$.$0^{9,13}$]pentadeca-3,10-dione systems for the formation of rearranged products.[2c,d] Besides, we are especially interested in studying the B–V oxidation of hexacyclo[10.2.1.$0^{2,11}$.$0^{4,9}$.$0^{4,14}$.$0^{9,13}$]pentadeca-3,10-dione (**5**) (X = CH_2, Y = Z = CO) and hexacyclo-

† NCL Communication No. 4529.

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