PART -- I SECTION - C

Toxicity (fungicidal and phyto-) of a series of α,β-unsaturated triorganostannyl carboxylates against some phytopathogenic fungi.

I.C-1: Studies on Toxicity of a Series of Unsaturated Triorganotin Carboxylates against Phytopathogenic Fungi

I.C-1.1: Introduction

In the earlier section (SECTION-A) of the thesis, preparation, spectroscopic characterisation and regioselective reaction with mercury(II) salts of some α,β-unsaturated (both olefinic and acetylenic) triorganostannyl esters have been presented. Since triorganotin carboxylates are known to exhibit a wide range of biological effects[1-3], some studies were undertaken to screen the fungicidal and phytotoxicity of a series of unsaturated triorganostannyl carboxylates during the course of the present study. As a prelude to the present work, it is necessary to describe a concise review on the previous applications of related compounds.

Organotin compounds after their discovery around 1850, long remained of purely scientific interest. A systematic investigation of the antifungal effectiveness of organotin compounds was started in 1950 by van der Kerk and Luijten[4]. They evidenced the high fungitoxicity of compounds of the type R_3SnX(triorganotin derivatives) compared to tetra- (R_4Sn), di- (R_2SnX_2), and mono-($RSnX_3$), substituted

organotin compounds. From their studies[5-7] with trialkyltin compounds(R_3SnX), the nature of the X group did not appear to have, in general, any particular effect on the activity. With regard to alkyl groups, e.g. with trialkyltin acetates($CH_3COO-SnR_3$), it was revealed that not the nature of the individual groups, but the total number of carbon atoms in the three groups was decisive. For a high antifungal toxicity the total number of carbon atoms in the alkyl groups of a trialkyltin compound should be about nine to twelve[6]. Thus dimethyloctyltin acetate(1) had the same high activity as tri-n-propyltin acetate(2) or as tri-n-butyltin acetate(3). They inhibited the growth of test fungi at concentration of 1mg/L or lower[5,8]. Tricyclopentyl(4) or tricyclohexyltin acetates(5) were more active than the n-alkyl derivatives[7].

$$CH_3-\overset{O}{\overset{\|}{C}}-O-SnR_2R^1$$

(1) R=Me, R^1=Octyl

(2) R = R^1 = n-Pr

(3) R = R^1 = n-Bu

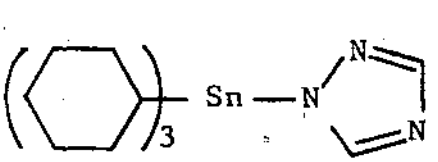
(4) R=R^1=Cyclopentyl

(5) R=R^1=Cyclohexyl

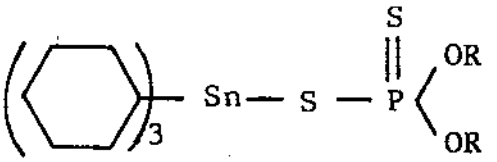
(6) R=R^1= Phenyl

In the case where R=aryl, introduction of functional groups did not lead to a significant improvement in activity over that of the unsubstituted triphenyltin derivative[5,9,10]. Triphenyltin acetate(6), the first agricultural organotin

fungicide(BRESTAN®), was developed by Hoechst in 1960[11,12]. Shortly afterwords, a second organotin fungicide, triphenyltin hydroxide, with a spectrum of activity similar to that of acetate[13], achieved commercialisation[3]. Among other triorganotin compounds, the major agricultural application was realised in tricyclohexyltin hydroxide(PLICTRAN)[14] and compounds(7)[15] and (8)[16].

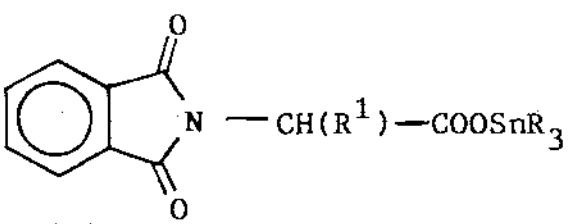


(7) Tricyclazole



(8) R-28627

Several articles on applications and biological effects of organotin compounds are available in the literature[1-3,17]. In the recent years, Shcherbakov & his workers[18] and M. Gielen & his associates[19,20] carried out investigation on the biological activity of trialkyltin esters of N-phthaloyl-protected amino acids(9) and triphenyltin carboxylates(10) of substituted salicylic acids[19] respectively.



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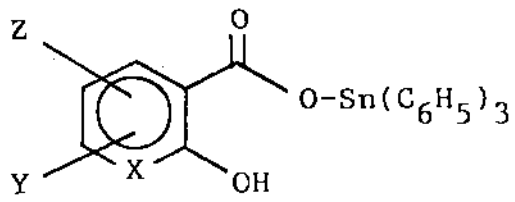


(10a) X=CH, Y=4-Me, Z=H

(10b) X=CH, Y=5-OMe, Z=H

(10c) X=CH, Y=5-NH_2, Z=H

(10d) X=CH, Y=5-SO_3H, Z=H

(10e) X=CH, Y=3-$CHMe_2$, Z=$CHMe_2$

(10f) X=N, Y= Z = H

Shcherbakov et al.[18] observed that their compounds were indicative of the average fungicidal activity[21]. However, the phthaloyl protection of the amino group increased to some extent the fungitoxicity relative to the organotin analogue with the unprotected amino group. In their studies with compounds(10a-10f), Gielen et al.[19] noticed that compounds(10c) and (10e) displayed highest toxicity against Gaeumannomyces graminis while compounds (10b) and (10c) were most toxic against Fusarium avenacearum fungi.

The principal advantages of the organotin agrochemicals (which mainly possess prophylactic action[22]) are their relatively low phytotoxicity, their generally low toxicity to

non-target organisms and the lack of resistance by crop pests to these chemicals. Furthermore, triorganotin compounds possessing relatively weak nature of Sn-C bond, undergo degradation in the environment, eventually to form harmless inorganic tin residues.

The mode of action or metabolism of organotin compounds has been the subject of much discussion. It was suggested [8,23] that inhibition of oxidative phosphorylation in the case of the trialkyltin compounds might be the case of the observed inhibition of fungal growth. In vivo animal studies, little informations were derived regarding the dealkylation or dearylation products formed from the organic moieties. However, work by Prough et al.[24] on the NADPH- and oxygen dependent microsomal metabolism of the ethylene series Et_nSnX_{4-n}(n=2-4) demonstrated that the major organic metabolite was ethylene and the minor product, ethane.

I.C-2: Present work: Results and discussion

From the preceding discussion it was evident that for trialkyltin acetates to exhibit antifungal activity, the nature of alkyl groups had a great role. At the same time, the influence of the nature of the carboxylate group on the activity was also studied[25]. In connection with our interest

with α, β -unsaturated triorganostannyl carboxylates, we focussed our attention on the fungicidal activities in vitro of the compounds(11-20). Early studies[26] on the fungitoxicity of unsaturated trialkyltin carboxylates, e.g., acrylate, methacrylate etc. were associated with a problem relating to their stability. These esters are known[27] to be polymerised even at room temperature. The tin carboxylates, comprised of the present investigation, were isolated in pure form conveniently and stable enough to conduct the biological studies. The in vitro tests of fungicidal activity of the organotin compounds have limited value to the organotin pesticide chemist unless their phytotoxicity are determined[3]. We also studied the phytotoxicity of these unsasturated triorganostannyl esters (11-20).

I.C-2.1: Biocidal Activity

The compounds(11-16) were screened for their fungicidal effectiveness in vitro against Alternaria solani and the esters(17-20) were screened against Piricularia oryzae. The poison food technique [28] was followed for testing and the growth inhibition was evaluated using the formula[29]: % inhibition=C-T/C x 100, where C and T are growth of fungus under control and treated plates respectively. All the carboxylates(11-16) were found to be active against A. solani

and compounds(17-20) against P. oryzae. The % of growth inhibition was measured at different concentration at different time (24hrs, 48hrs and 72hrs.) and the ED_{95} values were obtained by calculating these results by least square regression analysis. The results were summarised in TABLE I & II.

For phytotoxicity study of these unsaturated tin carboxylates(11-20), rice seeds were dipped in compound suspension at different concentration (25, 50 and 100 ppm) for one, four and eight hours. The treated seeds were allowed to germinate for eight days and germinated seeds were counted against control. The percentage of germinated seed at different concentrations and times were presented in TABLE-III.

From the results (ED_{95} values) in TABLE-I it was found that compound(11), the tri-n-butylstannyl crotonate, showed maximum inhibition after incubation for 24 hours and 72 hours while the tri-n-butylstannyl p-nitro cinnamate(15), inhibited the growth at 4.96 ppm after 48 hours against A. solani. On the other hand, triphenylstannyl crotonate(12) was found to be least active. From TABLE-II, triphenyltin but-2-ynoate(20), was the most active against P. oryzae after 24 hours incubation(1.95 ppm) and least active after 72 hours

incubation(12.87 ppm). The tri-n-butyltin cyclohexylidene acetate(18) inhibited the growth of the fungi (P. oryzae)with doses within the range 5.93-7.00 ppm, an average acitivity relative to other tin esters.

With regard to the assessment of phytotoxicity of these unsaturated tin carboxylates(11-20) (TABLE-III), it was revealed that tri-n-butylstannyl but-2-ynoate(19) did not have practically any phytotoxicity even at doses 100 ppm. The compounds(11) and (15) were most fungitoxic against A. solani, and at the same time their phytotoxic effects were almost nil. Again, the compound(20) exhibited highest fungicidal effectiveness and its phytotoxicity was nil. Among these esters studied, the tri-n-butylstannyl sorbate(13) showed highest phytotoxicity for 8 hours dipping at the concentration 50 and 100 ppm.

Despite the effectiveness of tripropyl- and tri-n-butyl-tin compounds in vitro, field trials demonstrated that not only are they very phytotoxic, but their ability to control fungi is reduced. In contrast, triphenyltins were found to be tolerated by the plants to a greater degree and were highly fungistatic. In our studied compounds, for example the tri-n-butylstannyl but-2-ynoate(19) and triphenyltin but-2-ynoate(20), the butyl group showed less phytotoxicity than the phenyl group. However, the

triphenyltin ester(20) exhibited most fungitoxicity (1.95 ppm for 24 hrs.) compared to the butyltin ester(19) (4.37 ppm for 24 hrs.) against P. oryzae.

I.C-3: Experimental

Materials and Methods

Antifungal Activities

i) Compounds: Tri-n-butylstannyl crotonate(11), Triphenylstannyl crotonate(12), Trin-butylstannyl sorbate(13), Triphenylstannyl sorbate(14), Tri-n-butylstannyl p-nitrocinnamate(15), Triphenylstannyl p-nitro cinnamate(16), Tri-n-butylstannyl cinnamate(17), Tri-n-butylstannyl cyclohexylidene acetate(18), Tri-n-butylstannyl but-2-ynoate(19), Triphenylstannyl but-2-ynoate(20) reported earlier in SECTION-A, and have been tested for fungitoxicity and phytotoxicity.

ii) Organisms:

a) Alternaria solani (EII and Mart) Jones and Grout -causal organism of early blight disease of potato.

b) Piricularia oryzae cav-causal organism of blast disease of rice.

iii) Culture media : Solid media[malt extract agar[30]]

20g malt extract (Difco) was boiled in water till dissolved. 20g agar agar(Kobe-Japan) was added and boiled until agar agar was well dissolved. 0.05g chloramphenicol was

suspended in 5 ml of 95% alcohol and added to the medium as antibacterial agent. The volume of the medium was then made upto 1 litre by addition of water, P^H of the medium was adjusted with sodium hydroxide to 6.5. Medium was sterilised at 15 p.s.i. for 20 minutes.

I.C-3.1:

Antifungal Activities of some α,β -Unsaturated Organotin carboxylates in vitro

Acetone solution of suitable quantity of the compounds(11-20) in sterile distilled water was incorporated into melted malt agar so as to get the desired concentrations of the compound in the media. Media with desired concentrations of compounds were poured in petriplates and after solidification were incubated at the centre with uniform discs(7 mm) of mycelia, punched out with a sterile cork borer from the advancing zone of the culture test fungus. Three replications on each test with appropriate control under same conditions were maitained. The petriplates were then incubated at 30±1°C in dark. Linear growth of the fungal discs were measured after regular interval and the percentage of growth inhibition over control was calculated and finally ED_{95} values(ppm) were recorded in TABLE I & II.

TABLE-I

Effect on growth of A. solani

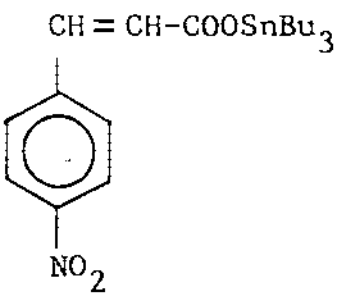
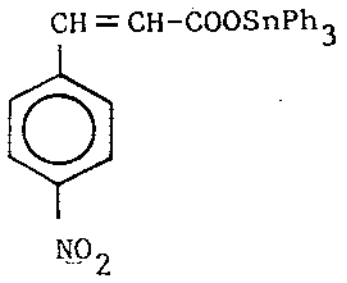
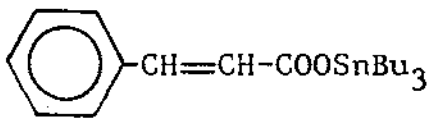
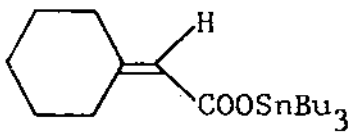
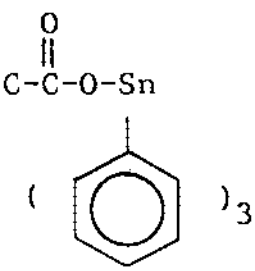
Compound	ED_{95} value(ppm) for incubation period		
	24hrs	48hrs	72hrs
(11) $CH_3-CH=CH-COOSnBu_3$	4.4	5.7	6.34
(12) $CH_3-CH=CH-COOSnPh_3$	9.92	10.00	10.00
(13) $CH=CH-COOSnBu_3$ $\vert$ $CH=CH-CH_3$	-	6.57	7.42
(14) $CH=CH-COOSnPh_3$ $\vert$ $CH=CH-CH_3$	-	5.74	5.80
(15) 	4.8	4.96	9.14
(16) 	9.24	9.36	10.00

TABLE-II

Effect on growth of P. oryzae

Compound	ED_{95} values(ppm) for incubation period		
	24hrs	48hrs	72hrs
(17) 	6.22	6.47	7.19
(18) 	5.93	6.50	7.00
(19) $CH_3-C\equiv C-COOSnBu_3$	4.37	8.45	9.22
(20) 	1.95	9.20	12.87

I.C-3.2: Phytotoxicity on Rice

i) Seed Sample :

Healthy rice seeds of PUSA 2-21 variety collected from Chinsurah Rice Research Farm, Hoogly, West Bengal were used in the investigation.

ii) Compound numbers (11-20)

iii) Effect on seed germination

Healthy rice seeds were dipped in compound suspension of 25, 50 and 100 ppm concentrations for 1, 4 and 8 hours. For control, water with requisite amount of acetone was used. The treated seeds were then placed on moist three layered filter paper in closed petriplates. Plates were incubated at 30 1°C. 100 seeds were maintained for each treatment. After 8 days the germinated seeds were counted. Seeds producing a root or a coleoptile were recorded as germenated. Three replications of each test with appropriate control under same conditions were maintained. The percentage of germinated seeds were counted with respect to control (results were placed in TABLE-III).

TABLE-III

Effect of the compounds on rice seed germination

Compound	Concn. (ppm)	% of germinated seeds with respect to control treated for		
		1hr	4hrs	8hrs
(11) Tri-n-butyltin crotonate	100	91	81	75
	50	93	83	82
	25	96	89	85
(12) Triphenyltin crotonate	100	91	88	88
	50	93	88	88
	25	98	90	89
(13) Tri-n-butyltin sorbate	100	83	79	66
	50	87	83	76
	25	96	95	79
(14) Triphenyltin sorbate	100	90	89	88
	50	92	90	88
	25	95	92	88
(15) Tri-n-butyltin p-nitro cinnamate	100	87	87	82
	50	89	91	90
	25	83	93	94
(16) Triphenyltin p-nitro cinnamate	100	86	88	81
	50	91	82	78
	25	95	90	83

Contd...

TABLE-III

Contd...

Compound	Conc^{n}. (ppm)	% of germinated seeds with respect to control treated for		
		1hr	4hrs	8hrs
(17) Tri-n-butyltin cinnamate	100	90	80	80
	50	91	82	78
	25	92	84	76
(18) Tri-n-butyltin cyclohexylidene acetate	100	100	93	90
	50	100	95	92
	25	100	96	93
(19) Tri-n-butyltin but-2-ynoate	100	100	100	98
	50	100	100	100
	25	100	100	100
(20) Triphenyltin but-2-ynoate	100	93	95	90
	50	97	95	91
	25	97	97	91

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Preliminary Communication

Selectivity of mercury(II) salts in reactions with α,β-unsaturated stannyl esters

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Abstract

Demetallation reactions of tri-n-butyltin carboxylates of some α,β-unsaturated carboxylic acids (acrylic, crotonic, cinnamic, sorbic and cyclohexylidene acetic) with mercury(II) salts (HgX_2; X = Cl, OAc) occurred selectively, and no mercuration of the olefinic double bond was detected.

1. Introduction

The mercuration of olefins (isolated/conjugated) with mercury(II) salts is a well documented reaction [1]. The resulting organomercurials have found many applications in organic synthesis [2]. For example, the preparation of serin [3] involves the solvomercuration of the carbon–carbon double bond of methyl acrylate upon treatment with mercuric acetate in methanol, whereas organotin carboxylates undergo demetallation with mercury(II) salts as reported by Roy *et. al* [4]. With these observations in mind, it is of interest to investigate the reactions between α,β-unsaturated stannyl carboxylates and mercury salts. We report here the difference in reactivity towards mercury(II) salts observed in the case of stannyl esters and their alkyl esters, and we believe that this portends certain potential in organic synthesis.

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2. Results and discussion

Our investigation embodied several types of α,β-unsaturated tin carboxylates of unsubstituted (acrylic), β-monosubstituted (crotonic, cinnamic and hexa-2,4-dienoic) and β,β-disubstituted (cyclohexylidene acetic) carboxylic acids. The reactions of these esters with

TABLE 1.

Entry	Tin carboxylates	HgX_2	Solvent	Time/Temp.	Yield [a] of BuHgCl (%)	Yield [a] of Acid (%).
1	$CH_2=CH-COOSnBu_3$ [b]	X = Cl	MeOH	48 h/r.t.	89	42
		X = Cl	CH_3CN	6 h/reflux	86	40
		X = OAc	MeOH	48 h/r.t.	84	30
		X = OAc	CH_3CN	6 h/reflux	82	42
2	$CH(CH_3)=CH-COOSnBu_3$ [b]	X = Cl	MeOH	48 h/r.t.	40	45
		X = Cl	PhH	4 h/reflux	88	43
		X = OAc	CH_3CN	4 h/reflux	96	47
		X = OAc	PhH	4 h/reflux	84	48
3	$CH(Ph)=CH-COOSnBu_3$ [b]	X = Cl	MeOH	48 h/r.t.	96	45
		X = Cl	CH_3CN	6 h/reflux	94	48
		X = OAC	MeOH	48 h/r.t.	85	46
		X = OAC	CH_3CN	6 h/reflux	90	49
4	$CH(CH=CH-CH_3)=CH-COOSnBu_3$ [c,e]	X = OAc	MeOH	48 h/r.t.	71	50
		X = Cl	PhH	4 h/reflux	76	43
		X = Cl	CH_3CN	6 h/reflux	92	59
5	 [d,e]	X = OAc	MeOH	48 h/r.t.	73	48
		X = Cl	PhH	4 h/reflux	78	44

[a] Yield of isolated pure product. [b] M.p. 69–70°C (Lit. [8] 69–70°C). [c] M.p. 84–85°C. [d] M.p. 80°C. [e] Compounds listed in entries 1, 4 and 5 gave satisfactory ^{1}H-NMR spectral data.

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mercuric chloride and mercuric acetate were studied in different solvents ranging from protic/aprotic polar to aprotic nonpolar (Table 1). In each case, butyl mercuric chloride and the corresponding acids were obtained after hydrolysis in fair to excellent yields. The formation of butyl mercuric chloride in the case of using mercuric acetate probably occurred [5] during washing of the reaction mixture with brine. Although change in the solvents did not significantly affect the yields of the products, the use of methanol, however, required a lower temperature. The results are summarised in Table 1.

While the alkyl esters of α,β-unsaturated acids, upon treatment with mercury(II) salts, undergo solvomercuration of carbon–carbon double bonds [2,3], the corresponding stannyl esters, upon similar treatment, react preferentially at the ester function keeping the olefin unreacted. Thus, by using the stannyl esters we were able to protect the carbon–carbon double bond and thereby provide a useful approach for preferential reactions of different functionalities in α,β-unsaturated esters towards mercury(II) salts. This method also provides a mild and neutral condition for hydrolysis of alkyl or aryl esters [6].

3. Experimental details

General procedure

To a solution of tri-n-butylstannyl carboxylates (2 mmol) in a solvent (10 ml) were added mercury(II) salt (2 mmol) (HgX_2; X = Cl, OAc) and the mixture was stirred under the conditions noted in Table 1. A small amount of white solids precepitated during the reaction which were filtered off. The filtrate was diluted with ether, and the organic layer was then washed with aqueous sodium chloride and dried over anhydrous Na_2SO_4. Evaporation of volatiles afforded the residue, which was crystallized from light petroleum to give BuHgCl as shining flakes in excellent yields.

M.p. 128°C (lit. [7] 127–130°C). ^{1}H-NMR (270 MHz, $CDCl_3$, ppm): δ 2.1 (t, 2H, J = 7.13 Hz), 1.78–1.67 (m, 2H), 1.48–1.34 (m, 2H), 0.95 (t, 3H, J = 7.29 Hz). ^{13}C-NMR (22.40 MHz, $CDCl_3$, ppm for APT spectra a (+) indicates 0 or 2 attached protons and a (−) indicates 1 or 3 attached protons): δ 33.06 (+), 30.09 (+), 27.81 (+), 13.47 (−). Anal. Found: C, 16.08; H, 3.17. C_4H_9HgCl calcd.: C, 16.38; H, 3.07%.

The mother liquor was diluted with ether and washed with saturated aqueous sodium bicarbonate. The aqueous phase was made acidic (3 N HCl) and extracted with ether. The organic phase was washed with aqueous sodium chloride, dried (Na_2SO_4) and evaporated to afford the corresponding acids, then recrystallized from benzene–light petroleum. Physical and spectral data of all acids isolated are identical with those of authentic samples.

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A mild and facile method for hydrolysis of esters†

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A mild method for the hydrolysis of primary, tertiary and aromatic esters through their corresponding triorganostannyl esters is reported.

A number of mild hydrolytic and non-hydrolytic approaches are available for masking and demasking of carboxyl group (alkyl, aryl, etc.)[1,2]. Despite this, the search is on for still milder methods to bring about the demasking of carboxylate groups. We present herein a new two-step sequence for deprotection of alkyl/aryl carboxylates under mild acidic condition.

In the first step the alkyl/aryl carboxylates are transesterified to the trialkylstannyl esters under completely neutral conditions, such as (i) by azeo-

Table 1—Characterization data of triorganostannyl carboxylates (**2**)

Entry No.	Esters **1** R^1-COO-	R^2	Solvent	Reflux time (hr)	Yield of **2** (%)[a]	m.p.[b] (°C) (Lit.)	IR[c] of **2** (C=O) in cm^{-1} (Nujol)	PMR[d] of **2** in δ (ppm) (J = Hz); Solvents[e]
1a	$Ph-CH=CH-COO-$	Me	CCl_4	12	80	71	1640	0.70-1.90 (m, 27H), 6.35 (d, 1H, J = 16), 7.10-7.60 (m, 5H), 7.56 (d, 1H, J = 16)
1b	$Ph-CH=CH-COO-$	Me	Ph·Me	12	93	"	"	"
1c	$Ph-CH=CH-COO-$	Me	Neat	12	82	"	"	"
2	$CH_3-CH=CH-COO-$	Et	CCl_4	12	95	81	1655	0.66-1.75 (m, 27H), 1.82 & 1.86 (two ds, 3H, J = 7), 5.63-6.15 (m, 1H), 6.61-7.20 (m, 1H)
3	CH_3-COO-	Et	CCl_4	12	82	85 (85)[5]	1575, 1555	0.70-1.90 (m, 27H), 1.95 (s, 3H)
4	CH_3-COO-	CH_2-Ph	CCl_4	12	90	"	"	"
5	CH_3-COO-	p-C_6H_4	CCl_4	24	96	"	"	"
6	$Me_2C(CH_2-COO-)(COO-)$	Me	Ph·Me	36	82	205-208(d)	1600, 1525 (KBr)	f
7	Betulinate[4]	Me	CCl_4	18	79	70-73	3430 (−OH), 1658, 1635 ($CHCl_3$)	0.86-2.08 (m, 67H), 2.18 (s, 3H), 4.43 (m, centered at, 1H), 5.88 (s, 1H), 6.13 (s, 1H)
8	$p-OH\cdot C_6H_4\cdot COO-$	Me	Neat	15	81	281(d)	1605	f, g
9	$H_2C(COO-)_2$	Et	CCl_4	12	65	85-87 (87)[5]	1585, 1565	0.66-1.90 (m, 54H), 3.18 (s, 2H)
10	$(H_2C)_4(COO-)_2$	Me	CCl_4	12	91	104-105 (105)[6]	1560, 1540	0.70-1.90 (m, 58H), 2.10-2.48 (m, 4H)

(a) Yield of isolated pure product; (b) Uncorrected; (c) Recorded on a Pye Unicam SP 3-300S spectrophotometer; (d) Recorded on Varian T-60 or EM-360 spectrometer using TMS as internal standard; (e) CCl_4 used for Entry No. 1-5 & 9 and $CDCl_3$ used for Entry No. 7 & 10; (f) PMR spectra could not be recorded because of poor solubility in $CDCl_3$, D_6-DMSO & D_6-Acetone; (g) Probably the p-OH group has been converted into p-$OSnBu_3$ as the product did not give colouration with $FeCl_3$.

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tropic distillation of esters **1** with bis-trialkyltin oxide in carbon tetrachloride or toluene or (ii) by heating their neat mixture. The corresponding triorganostannyl carboxylates **2** so formed undergo easy hydrolysis to acids **3** by treatment with dilute acid at room temperature (Table 1). In all the cases facile formation of stannyl esters and their facile hydrolysis are observed in overall excellent yields.

$$\underset{\mathbf{1}}{R^1COOR^2} + (n\text{-}Bu_3Sn)_2O \rightarrow \underset{\mathbf{2}}{R^1COOSn(n\text{-}Bu)_3} \rightarrow \underset{\mathbf{3}}{R^1COOH}$$

$$+ n\text{-}Bu_3OR^2 \qquad + n\text{-}Bu_3SnX\ (X = Cl, OAc)$$

R^1 = alkyl (primary, tertiary), aryl, α,β-unsaturated functions.
R^2 = alkyl, phenyl and benzyl groups.

Experimental

Transesterification of alkyl/aryl carboxylate **1**: *General procedure*

A solution of **1** and bis-tri-*n*-butyltin oxide (1:1 equivalent for monoesters) in carbon tetrachloride or toluene was heated under reflux for several hours (see Table 1) using a Dean-Stark water separator. The solvents were distilled off and the residue was chromatographed over silica-gel. Elution with 20-50% benzene-light petroleum afforded the tri-*n*-butylstannyl esters **2**.

The stannyl ester **2** was taken in dil. hydrochloric acid (5*N*) or in glacial acetic acid as a suspension and stirred overnight at room temperature. After removing the aqueous acids under reduced pressure the acid **3** was obtained either by extracting with ether or by crystallisation. The transformation was almost quantitative.

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