SYNTHESIS, CHARACTERIZATION AND ANTIFUNGAL ACTIVITY OF SOME TRIORGANOTIN α,ß-UNSATURATED CARBOXYLATES

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Abstract

Triphenyl and tributyl tin carboxylates of crotonic, 2,4-hexadienoic and 4-nitrocinnamic acids have been prepared, characterized by spectral analyses and their antifungal effectiveness as well as phytotoxicity have been evaluated.

Introduction

The evolution of organotin compounds as commercially important agricultural fungicides and insecticides has been well recognized[1-3]. The principal advantages of organotin agrochemicals (which mainly possess prophylactic action) are their relatively low phytotoxicity, their usually low toxicity to non-target organisms and eventual degradation in the environment to form harmless inorganic tin residues[4]. Taking account of the ability of tin carboxylates to act as potential antifungal reagents and in connection with our interests on α,β-unsaturated triorganostannyl carboxylates[5], we have focussed our attention on the biocidal activities of some unsaturated tin carboxylates. Here we report our results on the antifungal effectiveness in vitro of the compounds (**1-6**) as well as their phytoxicity on rice seed germination.

Experimental

Tributyltin carboxylates (**1,3 & 5**) and triphenyltin carboxylates (**2,4 & 6**) have been prepared by treatment of bis-tributyltin oxide or bis-triphenyltin oxide with a one molar proportion of the corresponding acid. Reactions were carried out in benzene or toluene with azeotropic removal of water. Confirmation of the structure of these tin carboxylates (**1-6**) came from their spectroscopic data.

Biocidal Activity

The compounds (**1-6**) were screened for their fungicidal effectiveness *in vitro* against *Alternaria solani*. The poison food technique[6] was followed for testing and the growth inhibition was evaluated using the formula: **% inhibition** = (C-T) / C x **100**, where C and T are growth of fungus under control and treated plates respectively. The ED_{95} values were calculated by least-square regression analysis and have been summarized in **TABLE-I**.

For phytotoxicity study of these unsaturated tin carboxylates, rice seeds were dipped in compound suspension at different concentrations (25-100 ppm) for one to eight hours. The treated seeds were allowed to germinate for eight days and germinated seeds were counted against control.

Results and Discussion

The IR spectra of the unsaturated organotin carboxylates (**1-6**) showed νmax (COO) absorption at 1500 -1655 cm^{-1}. However, these bands are probably associated[7] with the absorptions due to stretching vibration of both C-C double bond and the phenyl ring (compounds **2,4,5 & 6**). The 1H- and 13C- and 119Sn-NMR chemical shifts, alongwith coupling constant values (nJ(119Sn-13C)) (listed in **TABLE-II, III & IV** respectively) have been assigned on the basis of comparison with data for related organotin(IV) compounds[7,8] and found to be consistent with the suggested formulations. However, the detail interpretation of the spectral data with regard to their structural geometry will be discussed elsewhere.

All the tin carboxylates (**1-6**) are found to be active against *Alternaria solani* and out of these, compound (**5**) exhibited the highest activity after 48 hours incubation while compound (**4**) after 72 hours. On the other hand, phytotoxicity, studied on the germination of the seed (PUSA 2-21 variety), of compound (**5**) is found to be slightly higher than that of compound (**4**) (**TABLE-I**). This difference may, however, be attributable to the triphenyltin moiety in (**4**) and tributyltin moiety in (**5**) and is consistent with literature observation[9] that triphenyltin derivatives are observed to be tolerated by plants to a greater degree relative to the tributyltin compounds.

TABLE - I

Physical data, Antifungal Screening and Phytotoxicity Results

Compounds	Yields(%) [a]	MP(^{0}C)[b] (Lit)	νCOO[c] (cm^{-1}) (Nujol)	Fungitoxicity ED95 (ppm) Incubation Hr. 48	72	Phytotoxicity (% of Germinaed seed over control) Conc. 25-100 ppm Time 1-8 Hr.	
1. CH_3-CH=CH-COOSnBu_3	86 (84)[10]	81	1655(s), 1555(s) & 1535(s)	5.70	6.34	96	75
2. CH_3-CH=CH-COOSnPh_3	80	141-142	1650(s), 1570(m), 1545(s) & 1515(s)	10.0	10.0	98	88
3. CH=CH-COOSnBu_3 | CH=CH-CH_3	85	84-85	1625(m),1600(s) & 1500(s)	6.57	7.42	96	66
4. CH=CH-COOSnPh_3 | CH=CH-CH_3	79	96-98	1635(w),1610(m) & 1575(w)	5.74	5.80	95	88
5. CH=CH-COOSnBu_3 | C_6H_4-NO_2-4	84	76	1635(m),1595(s), 1563(s) & 1550(s)	4.96	9..14	94	82
6. CH=CH-COOSnPh_3 | C_6H_4-NO_2-4	88	178-179	1640(w),1610(m) & 1590(w)	9.36	10.0	95	81

a) Yields after crystallisation; b) Uncorrected; c) Pye Unicam SP3-300s SPECTROPHOTOMETER.

TABLE - II

1H-NMR Chemical Shifts and coupling constants [a,b]

Compound No.	δ (ppm) and J (Hz)
1.	6.84(m,βH); 5.84(dq,J=15.4&1.7,αH); 1.81(dq,J=6.9&1.7,CH_3); 1.74-1.54(m,6H,C2'); 1.20(m,12H,C1',&3'); 0.85(t,J=7.25,9H,C-4').
2.	7.89-7.62(m,6H,ArH); 7.50-7.37(m,9H,ArH); 7.06(m,βH); 5.97(dq,J=14.0&1.7,αH); 1.87(dq,J=6.9&1.7,CH_3).
3.	7.15(dd,J=15.2&13.7,βH); 6.21-5.96(m,2H,γ&δH); 5.79 (d, J= 15.2,αH); 1.80(d,J=6.1,CH_3); 1.72-1.53(m,6H,C-2'); 1.44-1.10(m,12H, C-1'&3'); 0.88(t,J=7.2,9H,C-4').
4.	7.80-7.53(m,6H,ArH); 7.40-7.13(m,10H,ArH & βH); 6.16-5.94(m,2H,γ&δH); 5.80(d,J=15.5,αH); 1.73(d,J=5.8,CH_3).
5.	8.20(dd,J=8.8&1.8,C-3&5H); 7.63(dd,J=8.8&1.8,C-2&6H); 7.59(d,J=15.9,βH); 6.58(d,J=15.9,αH); 1.71-1.57(m,6H,C-2'); 1.48-1.15(m,12H,C1'&3'); 0.90(t,J=7.2,9H,C-4').
6.	8.21(dd,J=8.8&1.8,C-3&5H); 7.83-7.78(m,6H,ArH); 7.75(d,J=16.2,βH); 7.63(dd,J=8.8&1.8,C-2&6H); 7.54-7.37(m,9H,ArH); 6.68(d,J=16.2,αH).

a) BRUKER NMR SPECTROMETER at 250MHz and in $CDCl_3$ solution. b) C-1' -- C4' correspond to protons on the Butyl group.

TABLE - III

13C-NMR Chemical shifts[a]

Compound No.	δ (ppm) COO	C-a	C-b	C-1'[b]/C-i	C-2'/C-o	C-3'/C-m	C-4'/C-p	Others
1.	171.81	124.3	143.22	16.41	27.67	27.02	13.62	17.75(CH_3)
2.	173.07	122.75	145.86	138.59	136.92	128.89	130.07	18.02(CH_3)
3.	172.46	120.87	144.19	16.46	27.68	27.02	13.61	18.51(CH_3), 130.10(C-γ), 137.58(C-δ).
4.	173.85	119.02	146.27	138.69	136.94	128.89	130.06d	18.68(CH_3), 130.06[d](Cγ) 39.07(C-δ).
5.	170.87	124.76	141.40	16.65	27.82	27.03	13.63	140.61(C1),128.40(C-2&6), 124.06(C-3&5),148.17(C4)
6.	171.99	124.15	142.38	138.04	136.93	129.06	130.37	140.96(C1),128.59(C-2&6), 123.15(C-3&5),148.40(C4).

a) BRUKER NMR Spectrometer at 62.89MHz and in CDCl3 solution, b) C-1' - C-4' correspond to the Carbon atoms of the Butyl groups, c) For triphenyl esters, the aromatic Carbon attached to Tin is *ipso*. d) Overlapped.

TABLE-IV

^{n}J(119Sn-13C), δ119Sn data

Compound No.	^{1}J(119Sn-13C)	^{2}J(119Sn-13C) (in Hz)	^{3}J(119Sn-13C)	119Sn[a] (δ in ppm)
1.	356.12	------	64.91	---------
2.	----	48.11	63.40	-182.66
3.	351.21	------	64.40	+106.58
4.	----	48.18	63.21	-160.85
5.	379.39	-----	64.53	+120.26
6.	----	48.30	63.65	-103.37

a) Chemical shifts were measured on a VXR-300S NMR spectrometer at 111.862 MHz in CDCl3 solution and relative to external tetramethylstannane.

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