

Structural and Biocidal Studies of Organotin(IV) Complexes of Triazene-1-Oxides

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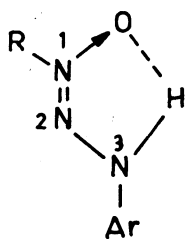
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Five co-ordinate and six co-ordinate complexes of triorganotin(IV) and diorganotin(IV) involving variedly substituted monobasic bidentate triazene-1-oxides (TH) have been synthesised. Trigonal bipyramidal structure for five co-ordinate and *trans*-diorgano octahedral structure for six co-ordinate complexes have been assigned on the basis of analytical data, conductance values, molecular complexities in freezing benzene IR and Mössbauer spectral data. Antibacterial activity of triazene-1-oxides, organotin(IV) compounds R_3SnX_2 and R_3SnX and organotin(IV) complexes of triazene-1-oxides R_2SnT_2 and R_3SnT were examined using Agar-plate diffusion technique. Following order of biocidal activity has been found :

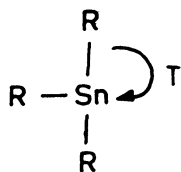


INTRODUCTION

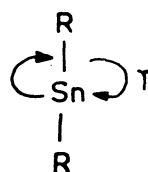
Co-ordination complexes of triazene-1-oxides have recently been reviewed¹. These ligands have only been used to explore the behaviour of phenylmercury(II)² in the study of the complexes of organometallic compounds. In the present communication an attempt has been made to study stereochemical disposition of Sn-C bonds in the diorganotin compounds in octahedral geometry besides the stereochemistry of five co-ordinate organotin(IV) complex. A comparative assessment of the biocidal activity of triazene-1-oxides, organotin compounds and their complexes has also been made. The ligands are represented by the general structure (I) and the substituents in the aromatic ring are indicated by using prefixes *o*-, *m*- and *p*- which are counted with respect to the N-C(Ar) bond. Five and six co-ordinate complexes are represented by the structures (II) and (III).



(I)



(II)



(III)

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EXPERIMENTAL

All chemicals used were of analytically pure grade unless otherwise specified. Triazene-1-oxides were synthesised by following published procedure³, *i.e.* by coupling the diazonium salt solution with substituted hydroxylamine at 0°C using sodium-acetate to control the pH of the reaction mixture. Ligands were purified by recrystallization from aqueous-ethanol. The starting materials for organotin(IV) compounds were anhydrous stannic chloride (0.05 mole), freshly distilled higher alkyl/aryl halides (0.2 mole), and freshly drawn sodium wire (10g). The reaction medium was dry boiling benzene. The reaction mixture was boiled for 2 hrs with occasional shaking. The mixture was filtered hot and the residue (NaCl) was extracted with hot benzene. Excess solvent was distilled off to get the tetraorganotin(IV) compounds. The organotin(IV) compounds were purified by recrystallisation from methyl acetate solvent. The reaction required absolutely dry benzene and dropwise addition of anhydrous stannic chloride (1 hr.). Iodination gave the organotin(IV) iodide derivatives and its metathetical reaction with equimolar thalous acetate gave the organotin(IV) acetate derivatives. Tri/di organotin(IV) iodide/acetate were made to react with variedly substituted triazene-1-oxide ligands in alcoholic medium in 1 : 1 and 1 : 2 molar ratios. The reaction mixture was refluxed for *ca.* 1/2 hr, filtered hot and cooled. Pale yellow organotin (IV) complexes came out on concentration and cooling. The complexes were recrystallised from acetone and dried over silica gel.

Nitrogen was estimated by following the method of Dumas. Tin was estimated as SnO_2 by decomposing the complex with HNO_3 . C, H and IR spectra in the range 4000–200 cm^{-1} were recorded at C.D.R.I, Lucknow CsI discs. 119 m Sn Mössbauer spectra were obtained using a constant acceleration spectrometer, the symmetrical triangular velocity drive waveform being derived from the multichannel analyser driven in the time mode by an external crystal controlled oscillator; 512 channels were used throughout. A 15 mCi $\text{Ca}^{119}\text{SnO}_3$ source was used at room temperature, and the samples were packed in perspex discs and cooled to 80 K using a continuous flow cryostat helium exchange gas. The spectrometer was calibrated using the magnetic splitting of an enriched Fe^{57} absorber foil. The data were folded to determine the zero velocity position, and the folded data fitted with Lorentzian functions by a least squares fitting programme⁵. The non-linearity of the spectrometer was determined, by a free fit of the Fe data, to be less than $\pm 0.06\%$. The quoted experimental error of $\pm 0.02 \text{ mm sec}^{-1}$ in the measured values of isomer shift and quadrupole splitting takes into account errors associated with non-linearities calibration, zero velocity determination and computer fitting⁶. Agar-plate diffusion technique⁷ was employed to determine the biocidal activity of triazene-1-oxide ligands, organotin(IV) iodide/acetate and their complexes. For this purpose filter paper/Whatman no.41) discs (5mm dia)

saturated with the solution of test compounds (10 mg/ml in acetone) were placed on the nutrient agar-plate (1.5g agar, 0.5% NaCl, 0.5% glucose and 2.5% pentane, all percentages being w/v between the pH range 6.8–7.0) after drying up the solvent. Each disc contained approximately 150 mg of the solvent. The plates were incubated at the optimum growth temperature of 37°C and the zones of inhibition around the discs measured after 24 hrs. All the experiments were carried out in duplicate. Following five species of bacteria were examined: *S. Aureus*, *S. Typhi*, *E. Coli*, *S. Faecalis* and *K. Pneumoniae*.

RESULTS AND DISCUSSION

Sixteen new compounds have been synthesised and studied. The characterisation data are tabulated in Table 1. From the characterisation data, it is obvious that the organotin(IV) complexes are non-electrolytes and monomers. The compounds are stable under ordinary conditions but the tendency to decompose increases with time. The consistent characterisation data even after repeated crystallisations at different intervals of time show that organotin(IV) complexes of triazene-1-oxides are not loose adducts, rather these are definite molecular addition compounds. R_2SnT_2 compounds were relatively more stable than R_3SnT compounds. This may be due to the more symmetrical six co-ordinate in octahedral environment rather than the five co-ordinate relatively unsymmetrical trigonal bipyramidal structure. Since tin(IV) has $4d^{10}$ electronic configurations, *i.e.*, with zero CFSE, the co-ordination number and stereochemistry of tin(IV) compounds is solely determined by the ionic size, electrostatic and covalent bonding forces⁸. Tin(IV) exhibits co-ordination numbers 4, 5 and 6, six co-ordination number being the most preferred one. This tendency is shown by the adduct formation of organotin(IV) halides by monodentate bases⁹ and bidentate ligands¹⁰.

Triazene-1-oxides show characteristic $\overset{3}{N}-H$ and $\overset{1}{N}-O$ bands¹¹⁻¹³ at about 3200 cm^{-1} and 1300 cm^{-1} respectively. On co-ordination $\overset{3}{N}-H$ bond disappears while $\overset{1}{N} \rightarrow O$ band is considerably lowered to 1250 cm^{-1} due to $\overset{1}{N} \rightarrow O \rightarrow M$ electron drainage. The characteristic single $Sn-C$ bond at 340 cm^{-1} shows the *trans* disposition of the two $Sn-C$ bonds. A *cis* configuration for the two $Sn-C$ bonds would have led to a splitting of $_{\text{asym}}Sn-C$ and $_{\text{sym}}Sn-C$ stretch as has been observed in bis(dithiocarbamato) di *p*-tolyle tin(IV)¹⁴ and similar other compounds¹⁵. Thus the IR spectral data testify to the co-ordination number five in R_3SnT and six in R_2SnT_2 . The logical structure for five co-ordinate tin(IV) is trigonal bipyramidal and *trans*-alkyl octahedral for six co-ordinate tin(IV), which is well in agreement with the single $_{\text{asym}}Sn-C$ band, absence of CFSE and the ionic size of tin(IV).

TABLE I
CHARACTERIZATION DATA OF ORGANOTIN COMPLEXES OF TRIAZENE-1-OXIDES

Compounds	Substituents		%C	%H	%N	%Sn	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)	Molecular weight
	R	Ar						
1. (C ₆ H ₅) ₃ SnT	CH ₃	C ₆ H ₅	59.80 (60.04)	4.31 (4.60)	8.26 (8.41)	23.21 (23.75)	2.0	502.30 (499.69)
2. (C ₆ H ₅) ₃ SnT	C ₆ H ₅	C ₆ H ₅	63.83 (64.09)	3.90 (4.45)	7.53 (7.48)	21.20 (21.13)	0.0	560.90 (561.69)
3. (C ₆ H ₅) ₃ SnT	CH ₃	C ₆ H ₄ Cl(p)	55.93 (56.17)	3.91 (4.12)	7.80 (7.86)	22.10 (22.22)	1.05	532.67 (534.14)
4. (C ₆ H ₅) ₃ SnT	C ₆ H ₅	C ₆ H ₄ Cl(p)	61.97 (62.05)	3.81 (4.14)	7.02 (7.24)	20.31 (20.46)	0.0	578.00 (580.14)
5. (C ₆ H ₅) ₃ SnT	CH ₃	C ₆ H ₄ CH ₃ (p)	60.46 (60.74)	4.39 (4.87)	8.03 (8.18)	23.09 (23.11)	0.0	508.02 (513.69)
6. (C ₆ H ₅) ₃ SnT	C ₆ H ₅	C ₆ H ₄ CH ₃ (p)	63.26 (64.62)	3.98 (4.69)	7.21 (7.30)	20.41 (20.62)	2.0	571.02 (575.69)
7. (C ₆ H ₅) ₃ SnT	CH ₃	C ₆ H ₅	54.10 (54.48)	4.13 (4.54)	14.70 (14.67)	20.61 (20.72)	1.0	568.13 (572.69)
8. (C ₆ H ₅) ₃ SnT	C ₆ H ₅	C ₆ H ₅	61.98 (62.01)	3.97 (4.31)	11.98 (12.06)	16.97 (17.04)	1.0	692.31 (696.69)
9. (C ₆ H ₅) ₃ SnT	CH ₃	C ₆ H ₄ Cl(p)	48.10 (48.63)	3.45 (3.74)	12.91 (13.02)	18.54 (18.50)	2.0	637.31 (641.59)
10. (C ₆ H ₅) ₃ SnT	C ₆ H ₅	C ₆ H ₄ Cl(p)	55.93 (56.43)	3.08 (3.66)	10.89 (10.67)	15.20 (15.50)	1.0	759.87 (765.59)
11. (C ₆ H ₅) ₃ SnT	CH ₃	C ₆ H ₅ CH ₃ (p)	55.60 (55.94)	4.67 (4.99)	13.89 (13.98)	19.50 (19.76)	2.0	596.32 (600.69)
12. (C ₆ H ₅) ₃ SnT ₂	C ₆ H ₅	C ₆ H ₅ CH ₃ (p)	62.85 (62.92)	4.32 (4.69)	11.49 (11.59)	16.27 (15.38)	1.0	719.98 (734.69)

Values in parentheses indicate the calculated values.

R and Ar are substituents to \dot{N} and \dot{N} atoms of the triazene-1-oxide.

Table 2 contains Mössbauer spectra data for the six co-ordinate organotin(IV) complexes together with data on some symmetrical bischelat

TABLE 2
MÖSSBAUER DATA (mm S⁻¹) AT 80°K

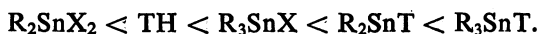
Complex	Substituents		C.S. ^{a,b}	Obs. q.s. ^b	Calc. q.s. ^c
	R	Ar			
SnPh ₂ (quin) ₂	—	—	1.04	3.50	(+) 3.70
SnMe ₂ (quin) ₂	—	—	1.08	3.27	(+) 3.92
(C ₆ H ₅) ₂ SnT ₂	CH ₃	C ₆ H ₅	1.04	3.73	—
(C ₆ H ₅) ₂ SnT ₂	C ₆ H ₅	C ₆ H ₅	1.02	3.50	—
(C ₆ H ₅) ₂ SnT ₂	CH ₃	C ₆ H ₄ Cl(p)	1.04	3.31	—
(C ₆ H ₅) ₂ SnT ₂	CH ₃	C ₆ H ₄ CH ₃ (p)	1.02	3.50	—
(C ₆ H ₅) ₂ SnT ₂	C ₆ H ₅	C ₆ H ₄ CH ₃ (p)	1.03	3.52	—
(C ₆ H ₅) ₂ SnT ₂	CH ₃	C ₆ H ₄ NO ₂ (p)	1.04	4.01	—
(C ₆ H ₅) ₂ SnT ₂	C ₆ H ₅	C ₆ H ₄ NO ₂ (p)	1.04	4.20	—

^a = ±0.05 mm S⁻¹, ^b = relative to BaSnO₃, ^c = Literature values.

R and Ar substituents refer to ¹N and ³N atoms in triazene-1-oxides.

late complexes. For the first two complexes the observed quadrupole splitting are also compared with calculated values based on the additivity model^{16,17} for *trans*-SnR₂ configuration. The centre shift (c.s.) and in particular, the quadrupole splitting (q.s.) values for all the diorganotin(IV) bischelates of triazene-1-oxides ranges between 3.31 to 4.20 mm S⁻¹. In the literature¹⁶, a *trans* label has been given to octahedral R₂SnX₄ compounds which show q.s. values in the range 3.37–4.32 mm S⁻¹. Although all the values of q.s. for complexes suggest *trans* octahedral configuration to the Sn—C bonds, it is shown that nitrosubstituents to the phenyl ring has the highest q.s. values and thus most symmetrical *trans* octahedral geometry. Mössbauer spectral data for five co-ordinate complexes is not available at the moment and will be communicated in the subsequent communication.

It is observed that R₂SnI₂ and R₂SnAc₂ are the least biologically active substances. The biocidal activity of TH is greater than these which in turn is less than R₃SnI and R₃SnAc. R₂SnT₂ have even greater biocidal activity relative to the aforesaid compounds but the most active biocidal ones are R₃SnT complexes. Thus an overall biocidal activity of the compounds studied is in the order:



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