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FORMATION OF ORGANOTIN–NITROGEN BONDS III*. *N*-TRIALKYLTIN-5-SUBSTITUTED TETRAZOLES

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N-Trialkyltin-5-substituted tetrazoles were prepared by the 1,3-dipolar cycloaddition of trialkyltin azides to nitriles and by the reaction of 5-substituted tetrazoles with bis(tri-n-butyltin) oxide or trimethyltin hydroxide. Both reactions gave a single product in which the trialkyltin group is attached to the 2-nitrogen of the tetrazole ring. Measurement of the viscosity showed that *N*-(tri-n-butylstannyl)-5-alkyltetrazoles were polymeric in fairly concentrated solutions. The nature of the tin–nitrogen bonding in the polymeric structure is discussed.

In contrast to the great reactivity of organotin–nitrogen bonds in organotin amides towards proton-releasing substances[1,2], such bonds in *N*-trialkyltin derivatives of imidazoles, 1,2,4-triazoles, benzimidazoles, benzotriazoles and azides bearing π-electron-withdrawing groups are less reactive[3–6], so that they do not undergo hydrolysis in water at room temperature. The high viscosities of toluene solutions of *N*-(tri-n-butylstannyl)imidazole and -1,2,4-triazole with two nitrogens in 1,3-positions indicates that they have polymeric structures in which the tin atom is five-coordinated even in solution[6]. Similar properties and structures were to be expected for *N*-trialkyltin derivatives of tetrazoles.

Since 5-substituted tetrazoles can be readily made by the 1,3-dipolar cycloaddition to nitriles of ammonium azide[7], aluminium azide[8,9], or trimethylsilyl azide[10,11], and 1,2,3-triazole derivatives by the similar addition of tri-n-butyltin azide to diethyl acetylenedicarboxylate[12], we have studied the properties of *N*-trialkyltin-5-substituted tetrazoles. We have found that the 1,3-dipolar cycloaddition of trialkyltin azides to nitriles occurs quantitatively to give *N*-trialkyltin-5-substituted tetrazoles, (I)–(XI). Since trialkyltin azide is thermally very stable[13,14] and readily prepared by the reaction of sodium azide with trialkyltin halide[5], the procedure may constitute a useful preparative method for tetrazoles. It is reported[15] that the addition of organic azides to nitriles occurs only when a strongly electronegative group is attached to the cyano group. By contrast, trialkyltin azide reacted more readily with a nitrile containing an electron-releasing substituent than with those containing electron-withdrawing groups. Treatment of the products with hydrogen chloride gave

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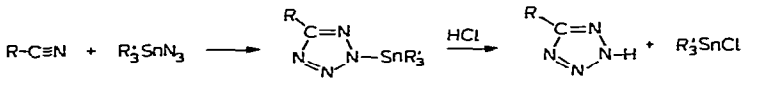
* For Part II see ref. 1.

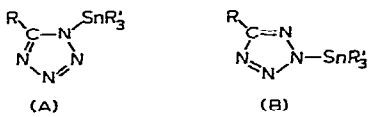
the corresponding free 5-substituted tetrazoles along with trialkyltin chloride being recovered. In general, *N*-trialkyltin-5-substituted tetrazoles were stable on exposure to air and water, except for *N*-(trialkylstannyl)-5-vinyltetrazole, which was slowly hydrolyzed in the air.



(I)–(XI)

	R	R'		R	R'
(I)	CH_3	n-C_4H_9	(VII)	p-$O_2NC_6H_4$	n-C_4H_9
(II)	C_2H_5	n-C_4H_9	(VIII)	p-$CH_3C_6H_4$	n-C_4H_9
(III)	n-C_3H_7	n-C_4H_9	(IX)	p-$CH_3OC_6H_4$	n-C_4H_9
(IV)	$C_6H_5CH_2$	n-C_4H_9	(X)	CH_3	CH_3
(V)	CH_2=CH	n-C_4H_9	(XI)	C_6H_5	CH_3
(VI)	C_6H_5	n-C_4H_9			

There are two possible structural isomers for (I)–(XI): the 1-trialkyltin-5-substituted tetrazole (A) and the 2-trialkyltin isomer (B). The cycloaddition gave a single product, as shown by the NMR and/or UV spectra. In the NMR spectrum of (I) for example, a single absorption assigned to 5-methyl protons, was found at 2.54 ppm. There was found a single absorption maximum (and any shoulder was absent) in the UV spectra of (VI)–(IX) and (XI), and the dipole moments and UV and NMR analyses were in favour of structure (B).



(A) (B)

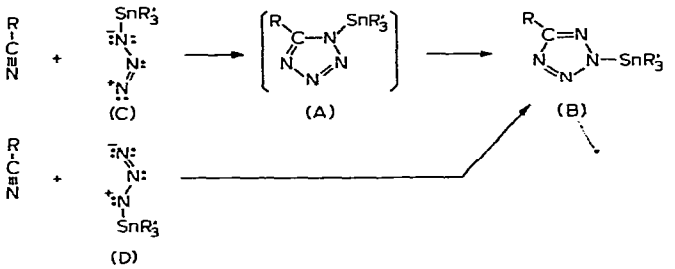
It was observed that 1-substituted tetrazoles have higher dipole moments than 2-substituted isomers; thus that of 1-methyl-5-phenyltetrazole (XIV) is 5.70 D, 1-ethyltetrazole 5.46 D, and 2-ethyltetrazole 2.65 D[16]. The relatively lower dipole moments of (I) (2.53 D) and (VI) (3.72 D) supported structure (B).

The absorption maximum for (VII) was observed at 302 nm, which is a far longer wavelength than those for nitrobenzene (λ_{max} 268 nm) and 1-methyl-5-(*p*-nitrophenyl)tetrazole (XVI)*[17], (λ_{max} 269 nm). When the bulky tri-n-butyltin group is attached to the 1-nitrogen atom, such a hypsochromic shift should be observed because the coplanarity of the two aromatic rings should be hindered by the tri-n-butyltin group. The NMR chemical shifts for the *ortho*- and *meta*-protons of (VII) were quite similar to those for the 2-methyl isomer (XVII) (Table 1). The *ortho*-protons were markedly deshielded by the anisotropic effect of the coplanar tetrazole ring in (VII) and (XVII). The UV and NMR spectra of (VI), (VIII) and (IX) were found to have

* The interplanar angle of twist between the ring-planes in (XVI) has been calculated as 28° by Braude's equation[18].

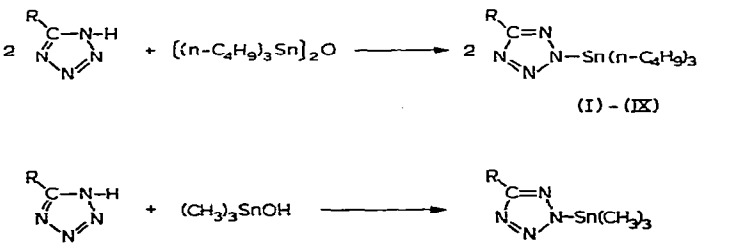
the analogous relation to those of (VII) supporting structure (B) (Table 1). In the case of (I)–(V), where there is no aryl substituent on 5-carbon, structural information was not obtained from UV and NMR spectra but instead from the dipole moments.

Two routes are possible for the formation of the structure (B). When trialkyltin azide has the 1,3-dipolar resonance structure shown in (C), cycloaddition should give the 1-trialkyltin isomer (A). Migration of the trialkyltin group from 1-nitrogen (A) to 2-nitrogen (B) might be possible; Birkofer and Wegner[19] reported a similar migration of the trimethylsilyl group in the reaction of trimethylsilyl azide with acetylene compounds to give 2-(trimethylsilyl)-1,2,3-triazoles.



Analogous behaviour has been found in the reaction of acetylene compounds with tri-n-butyltin azide to give 2-(tri-n-butylstannyl)-1,2,3-triazoles, which could not be formed without the migration of tri-n-butyltin group from 1-nitrogen to 2-nitrogen[20]. If cycloaddition occurred with trialkyltin azide having another 1,3-dipolar structure (D), the 2-trialkyltin isomer (B) would be produced directly. The available data are not sufficient at present to lead to a definite conclusion about the reaction mechanism.

Treatment of 5-substituted tetrazole with bis(tri-n-butyltin) oxide in ethanol gave as the sole product the corresponding 2-tri-n-butyltin-5-substituted tetrazole whose IR, NMR and UV spectra were superimposable on those of the compounds prepared by the 1,3-cycloaddition of tri-n-butyltin azide to nitrile. Analogous treatment of the tetrazoles with trimethyltin hydroxide gave 2-trimethyltin derivatives. Of the trimethyltin derivatives prepared [(X)–(XIII)], only (XII) was obtained as a monohydrate. This can be accounted for by the polarity of the tin–nitrogen bond in (XII) induced by the strongly electron-withdrawing *p*-nitrophenyl group. There was no reaction between lithium or sodium 5-phenyltetrazolate and tri-n-butyltin chloride.



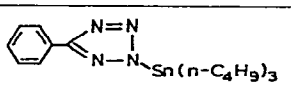
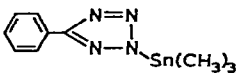
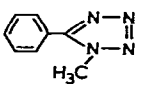
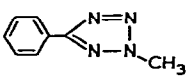
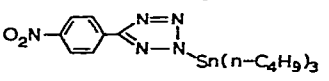
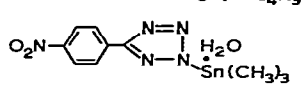
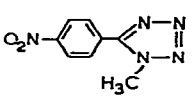
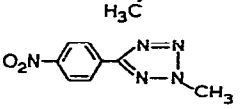
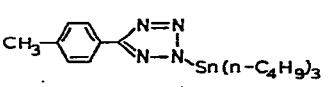
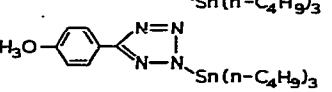
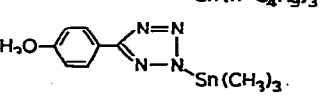
(XII) R = *p*-$O_2NC_6H_4$

(XIII) R = *p*-$CH_3OC_6H_4$

The viscosity of the toluene solution of *N*-(tri-n-butylstannyl)-5-alkyltetrazoles, (I)–(IV), was found to be highly dependent on concentration (Fig. 1), indicating, as was reported for the imidazole derivatives[6], that these compounds have polymeric structures containing pentacoordinated tin atoms even in toluene solution. Among the four possible polymeric structures (1,3-, 1,4-, 1,2- and 2,3-structures), the 1,3-structure (E) seems the most probable. As indicated in (E), the bond between 1-nitrogen and tin may possibly be weaker and longer than that between the 3-nitrogen and tin atoms. Since the tri-n-butyltin group has been shown to be attached to the 2-nitrogen, the 1,4-structure can be excluded. Both the 1,2- and 2,3-structures are improbable, because low viscosity was found in the case of *N*-(tri-n-butylstannyl)-

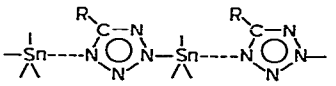
TABLE 1

ULTRAVIOLET AND NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA FOR *N*-SUBSTITUTED-5-ARYLTETRAZOLES

No.	Compound	UV (in C_2H_5OH)		NMR (in $CDCl_3$)	
		λ_{max} (nm)	ε_{max}	$\delta(H_o)$	$\delta(H_m)[\delta(H_p)]$
(VI)		242	13,800	7.72	7.40
(XI)		242	12,400	8.05[a]	7.38[a]
(XIV)		232[c]	11,500	7.64[b]	7.64[b]
(XV)		239[c]	14,900	8.13[b]	7.41[b]
(VII)		302	14,800	8.31	8.31
(XII)		302	13,600	8.23[a]	8.23[a]
(XVI)		269	14,100	8.05[b]	8.56[b]
(XVII)		282	16,500	8.21[b]	8.21[b]
(VIII)		244	15,900	7.76	7.27
(IX)		250	15,300	7.79	6.95
(XIII)		254	17.900	7.88[a]	6.93[a]

[a] Measured in methanol with DSS as an internal standard. [b] Data from ref. 17. [c] *Cf.* ref. 18.

pyrazole[6], 2-(tri-n-butylstannyl)-4,5-diethyl-1,2,3-triazole and 2-(tri-n-butylstannyl)-4-phenyl-1,2,3-triazole[20].



(E)

The dependence of the viscosity of solutions of 2-(tri-n-butylstannyl)-5-phenyltetrazole (VI) on the concentration was less than with (I)–(IV). Smaller viscosity increases were found in the case of 2-(tri-n-butylstannyl)-5-(*p*-nitrophenyl)tetrazole (VII) and -5-*p*-(methoxyphenyl)tetrazole (IX), and these may be monomeric even in concentrated toluene solutions (0.3 mol/l). Bonding between 1-nitrogen and tin in (E) is thought to be negligible in the case of (VII). Obviously, aryl groups attached to the 5-carbon of the tetrazole ring lead to decreased viscosity and increase the tendency towards monomeric structures, presumably by steric and inductive effects. The order of the Taft's σ_I value[21] of the *p*-substituents [H, CH_3 (0.00) < CH_3O (+0.25) < O_2N (+0.63)] parallels that of the lowering of the viscosity in Fig. 1, while the σ_p value[21] shows less agreement [CH_3O (−0.27) < CH_3 (−0.17) < H (0.00) < O_2N (+0.78)].

Since the *N*-trimethyltin derivatives, (X)–(XIII), are insoluble in non-polar solvents as toluene, their viscosities and dipole moments were not measured. In the IR spectra of (X)–(XIII), the absorption band at 500 cm^{-1} associated with the symmetric stretching vibration of an C–Sn–C linkage[22] was absent, so the trimethyltin group must be planar and pentacoordinate in the crystalline state. The UV spectrum of (XI) had an absorption maximum at similar wavelength as those of (VI) and (XV) (Table 1). This suggested that the trimethyltin group was attached to the 2-nitrogen atom in (XI), as in the case of the tri-n-butyltin derivatives. Similarly, the UV and NMR spectra are in favour of the structure (B) for (XII) and (XIII). The fact that the *N*-trimethyltin derivative (X) is undistillable might be an indication that the tin–nitrogen bond in it is more polar than that in the distillable *N*-tri-n-butyltin isomer (I).

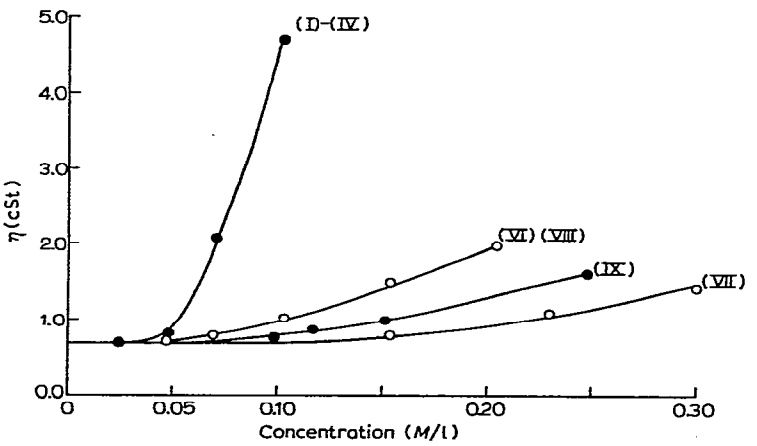


Fig. 1. The viscosity of toluene solutions of *N*-tri-n-butyltin-5-substituted tetrazoles.

EXPERIMENTAL

NMR spectra were measured in deuteriochloroform with a Japan Electron Optics C-60-H Spectrometer operating at 60 MHz. Chemical shifts are given in ppm downfield from internal tetramethylsilane.

The UV spectra were measured in ethanol on the Shimazu-MPS spectrophotometer.

The viscosities of toluene solutions were measured at $20° \pm 0.1°$ as described by Janssen, Luijten and van der Kerk[6]. The results are shown in Fig. 1.

Dipole moment

The dipole moments of (I) and (VI) were determined by measuring the dielectric constants and densities of benzene solutions at 25°. Since the concentrations of the benzene solutions were less than 0.05 mole/l, the solutes (I) and (VI) might be monomeric in benzene in the light of the viscosity measurements in toluene. Dielectric constants were determined by using a heterodyne beat capacitance apparatus[23] made by Dr. N. Koizumi's group at the Institute for Chemical Research, Kyoto University. The cell consisted of two concentric cylinders of platinum tubing sealed into a glass cylindrical vessel. The apparatus was calibrated with benzene, the dielectric constant of which was taken to be 2.2725 at 25°. Densities were determined with a Lipkin type pycnometer. Refractive indices of solution for Na_D light were measured with a Pulfrich refractometer and the molar refraction R_D calculated therefrom. Solute polarization was calculated from the Halverstadt and Kumler[24] relationship, and the dipole moment, μ, was calculated from the Debye equation:

$$\mu = 0.01281\,[(P_{2\infty} - R_2)\cdot T]^{\frac{1}{2}} \text{ Debye}$$

TABLE 2

CALCULATED DATA FOR DIPOLE MOMENTS

Compound	α	β	$P_{2\infty}$	R_2	μ
(I)	1.95	−0.320	227.9	96.7	2.53
(VI)	3.70	−0.349	405.6	121.9	3.72

2-(Tri-n-butylstannyl)-5-methyltetrazole (I)

Method A. A representative procedure is as follows. A mixture of 16.6 g (0.050 mole) of tri-n-butyltin azide[4] and 40 ml of acetonitrile was heated at 100° for 10 h in a sealed glass tube until the azide band at 2060 cm^{-1} in the IR spectrum had disappeared. The mixture formed two layers. Excess acetonitrile was evaporated off to give 18.6 g (100%) of a pasty liquid, which crystallized on standing overnight, m.p. 43–49°. High vacuum distillation gave 14.6 g of (I), b.p. 160°/0.008 mm, m.p. 49–50°. NMR: singlet 2.54 (3 H, 5-methyl protons), multiplet 0.7–1.7 (27 H, n-butyl protons). No UV absorption at 210–340 nm. (Found: C, 45.32; H, 8.30; N, 14.74. $C_{14}H_{30}N_4Sn$ calcd.: C, 45.07; H, 8.10; N, 15.02%.)

To an ethereal solution of 2.663 g (0.00702 mole) of (I) was added 20 ml of a saturated ethereal solution of anhydrous hydrogen chloride; colourless needles were formed. Ether and hydrogen chloride were evaporated off *in vacuo*, and the tri-n-

butyltin chloride formed was extracted three times with benzene. The crystalline residue, insoluble in benzene, was 5-methyltetrazole (0.580 g, 99%), m.p. 146–147° (lit.[25] m.p. 148–148.5°), which was identified by IR and NMR spectra, mixed melting point, and elemental analysis. Tri-n-butyltin chloride was isolated from the benzene solution in quantitative yield (2.312 g).

Method B. A representative procedure is as follows: A mixture of 5-methyltetrazole (0.0421 g, 0.502 mmole) and freshly distilled bis(tri-n-butyltin) oxide (0.1490 g, 0.251 mmole) was dissolved in anhydrous ethanol and heated to reflux for 10 min. Removal of ethanol *in vacuo* gave 0.1869 g (100%) of a pasty liquid whose IR and NMR spectra were superimposable on those of (I) prepared by *Method A*.

Analogous treatment of 5-substituted tetrazoles with bis(tri-n-butyltin) oxide gave the corresponding 2-tri-n-butyltin-5-substituted tetrazoles, (II)–(IX) in quantitative yields. Detailed descriptions of the preparation of (II)–(IX) by *Method B* are omitted.

2-(*Tri-n-butylstannyl*)-5-*ethyltetrazole* (*II*)

Analogous treatment of propionitrile with tri-n-butyltin azide gave (II) quantitatively, b.p. 157°/0.006 mm, n_D^{20} 1.5100. NMR: quartet 2.95 (2 H, methylene protons), triplet 1.42 (3 H, methyl protons), multiplet 0.7–1.7 (27 H, n-butyl protons). (Found: C, 46.61; H, 8.21; N, 14.27. $C_{15}H_{32}N_4Sn$ calcd.: C, 46.54; H, 8.33; N, 14.47%.) Treatment of (II) with hydrogen chloride in ether afforded 5-ethyltetrazole, m.p. 96–97° (lit.[25] 98–99°).

2-(*Tri-n-butylstannyl*)-5-*propyltetrazole* (*III*)

Reaction of n-butyronitrile with tri-n-butyltin azide gave (III), b.p. 180°/0.009 mm, n_D^{20} 1.5056. NMR: triplet 2.88 (2 H, methylene protons adjacent to tetrazole ring). (Found: C, 48.58; H, 8.68; N, 13.54. $C_{16}H_{34}N_4Sn$ calcd.: C, 47.90; H, 8.52; N, 13.94%.) Treatment of (III) with hydrogen chloride gave 5-n-propyltetrazole, m.p 62–63° (lit.[25] 64–65°).

2-(*Tri-n-butylstannyl*)-5-*benzyltetrazole* (*IV*)

Reaction of benzyl cyanide with tri-n-butyltin azide gave (IV), m.p. 74–74.5° (from ethanol). NMR: singlet 7.23 (5 H, phenyl protons), singlet 4.32 (2 H, methylene protons), multiplet 0.7–1.7 (27 H, n-butyl protons). (Found: C, 53.32; H, 7.76; N, 12.21. $C_{20}H_{34}N_4Sn$ calcd.: C, 53.37; H, 7.84; N, 12.44%.) 5-Benzyltetrazole was obtained by treatment of (V) with hydrogen chloride, m.p. 125–126° (lit.[25] 125.5–126°).

2-(*Tri-n-butylstannyl*)-5-*vinyltetrazole* (*V*)

A solution of 3.81 g (0.0115 mole) of tri-n-butyltin azide, 3 ml of freshly distilled acrylonitrile and 0.041 g of hydroquinone in 10 ml of benzene was heated at 80° for 7 h under dry nitrogen. Benzene and excess acrylonitrile was evaporated off to give a brownish pasty liquid, which was dissolved in diisopropyl ether. An insoluble reddish oil (0.602 g) was separated by decantation and the pale-yellow polymeric material floating in the solution was filtered off. Evaporation of the solvent from the filtrate gave 4.28 g (97%) of pale yellow practically pure (V) as a paste, which on exposure to air was hydrolyzed slowly to give 5-vinyltetrazole and bis(tri-n-butyltin) oxide. The latter was converted into tri-n-butyltin carbonate[1].

The NMR spectrum of (V) had an ABC pattern: quartet 6.75 (1 H, vinyl H_a of $H_a>C=C<^{H_c}_{H_b}$, J_{ab} 10 Hz, J_{ac} 16 Hz), quartet 5.63 (1 H, H_b, J_{bc} 3 Hz), quartet 6.28 (1 H, H_c). (Found: C, 44.83; H, 7.57; N, 13.95. $C_{15}H_{30}N_4Sn$ calcd.: C, 44.78; H, 7.85; N, 14.55%.) Attempts at further purification by distillation were not successful because decomposition and polymerization occurred. On exposure to light, (V) polymerized slowly.

A solution of 0.569 g (1.46 mmole) of freshly prepared (V) in 5 ml of diisopropyl ether was treated with 5.0 ml of ether containing 1.50 mmole of anhydrous hydrogen chloride. The reaction mixture was evaporated to give colourless crystals and a liquid. Extraction of the liquid with petroleum ether (b.p. 30–40°) left 0.112 g (81%) of crystalline 5-vinyltetrazole, m.p. 130–132° (lit.[9] m.p. 126–127°), which was identified by elemental analysis and by comparing the NMR and IR spectra[9] with those of an authentic sample.

2-(*Tri-n-butylstannyl*)-5-*phenyltetrazole* (*VI*)

Reaction of benzonitrile with tri-n-butyltin azide was carried out at 100° for 10 h to give oily (VI) which crystallized on standing overnight, m.p. 66–67° (from acetonitrile). The UV and NMR spectra are shown in Table 1. (Found: C, 52.40; H, 7.27; N, 12.61. $C_{19}H_{32}N_4Sn$ calcd.: C, 52.44; H, 7.41; N, 12.88%.) Treatment of (VI) with hydrogen chloride afforded 5-phenyltetrazole[7], m.p. 219–220° (lit.[25] 217–218°). UV: λ_{max} 240 nm, ε_{max} 15,300. NMR: $\delta(H_o)$ 8.07; $\delta(H_{m,p})$ 7.59; [lit.[17] $\delta(H_o)$ 8.10; $\delta(H_{m,p})$ 7.51].

2-(*Tri-n-butylstannyl*)-5-(*p-nitrophenyl*)*tetrazole* (*VII*)

A solution of 1.61 g (0.0108 mole) of *p*-nitrobenzonitrile and 2.99 g (0.0090 mole) of tri-n-butyltin azide in 20 ml of benzene was heated to reflux. After 50 h, the azide band at 2060 cm^{-1} had disappeared in the IR spectrum. Benzene was distilled off to give reddish yellow crystals which were extracted with diisopropyl ether. The extract was concentrated and cooled to give 1.95 g (45%) of crystals, m.p. 103–113°. Recrystallization from a mixture of diethyl ether and diisopropyl ether (1/5) gave pale yellowish cubic crystals of (VII), m.p. 112–114°. The UV and NMR spectral data are shown in Table 1. (Found: C, 47.59; H, 6.78; N, 14.72. $C_{19}H_{31}N_4O_2Sn$ calcd.: C, 47.53; H, 6.51; N, 14.59%.)

Treatment of (VII) with hydrogen chloride afforded 5-(*p*-nitrophenyl)tetrazole, m.p. 226–227° (lit.[7] 220–222°), which was identified by the mixed melting point and by comparing the IR, UV and NMR spectra with those of the authentic sample[7,17].

2-(*Tri-n-butylstannyl*)-5-*p-tolyltetrazole* (*VIII*)

Treatment of *p*-tolunitrile with tri-n-butyltin azide gave (VIII), n_D^{20} 1.5467. NMR: doublet 7.76 (2 H, *ortho*-protons respect to tetrazole ring, $J_{o,m}$ 8.4 Hz), doublet 7.27 (2 H, *meta*-protons), singlet 2.34 (3 H, methyl protons). UV: λ_{max} 244 nm, ε_{max} 15,900. (Found: C, 53.40; H, 7.75; N, 12.32. $C_{20}H_{34}N_4Sn$ calcd.: C, 53.37; H, 7.84; N, 12.44%.)

Treatment of (VIII) with hydrogen chloride in ether gave 5-*p*-tolyltetrazole, m.p. 242–243° (lit.[25] 250–250.5°).

2-(*Tri-n-butylstannyl*)-5-(*p-methoxyphenyl*)*tetrazole* (*IX*)

Treatment of *p*-methoxybenzonitrile[26] with tri-n-butyltin azide in benzene at 100° for 60 h gave oily (IX). NMR: doublet 7.79 (2 H, *ortho*-protons respect to tetrazole ring), doublet 6.95 (2 H, *meta*-protons), singlet 3.86 (3 H, methoxy protons). UV: λ_{max} 250 nm, ε_{max} 15,300. (Found: C, 51.36; H, 7.67. $C_{20}H_{34}N_4OSn$ calcd.: C, 51.64; H, 7.37%.)

Treatment of (IX) with anhydrous hydrogen chloride in ether gave 5-(*p*-methoxyphenyl)tetrazole, m.p. 237–238° (decomp.) (lit.[27], 228° (d)).

2-(*Trimethylstannyl*)-5-*methyltetrazole* (*X*)

A tetrahydrofuran solution of 2.00 g (0.0097 mole) of trimethyltin azide[4] and 1.64 g (0.040 mole) of acetonitrile was heated in a sealed glass tube at 77–80° for 14 h under dry nitrogen. Tetrahydrofuran and acetonitrile were evaporated off to give 2.3 g (96%) of colourless crystals, m.p. 215–216° (with sublimation). NMR: singlet 2.55 (3 H, 5-methyl protons), singlet 0.89 (9 H, tin-methyl protons) accompanied by small satellite peaks [$J(^{117}Sn–CH_3)$ 66 Hz, $J(^{119}Sn–CH_3)$ 69 Hz]. IR (KBr tablet): 545 cm^{-1} [ν_{as}(C–Sn–C)], absence of ν_s of C–Sn–C at ca. 500 cm^{-1}. (Found: C, 24.55; H, 5.04; N, 22.90. $C_5H_{12}N_4Sn$ calcd.: C, 24.34; H, 4.90; N, 22.71%.)

2-(*Trimethylstannyl*)-5-*phenyltetrazole* (*XI*)

A solution of 2.00 g (0.0097 mole) of trimethyltin azide[4] and 4.12 g of benzonitrile in 10 ml of tetrahydrofuran was heated at 80° for 14 h in a sealed glass tube. After tetrahydrofuran was evaporated, benzonitrile was extracted three times with diisopropyl ether to leave 2.7 g (91%) of colourless crystals, m.p. 211–212°. IR (KBr): 548 cm^{-1} [ν_{as}(C–Sn–C)], absence of ν_s(C–Sn–C) at ca. 500 cm^{-1}. NMR [in methanol, and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal standard]: quartet 8.05 (2 H, *ortho*-protons), triplet 7.47 (3 H, *meta*-, *para*-protons), singlet 0.72 (9 H, tin-methyl protons) accompanied by satellite peaks [$J(^{117}Sn–CH_3)$ 64, $J(^{119}Sn–CH_3)$ 66 Hz]. UV: λ_{max} 241 nm, ε_{max} 14,800. (Found: C, 38.68; H, 4.68; N, 18.09. $C_{10}H_{14}N_4Sn$ calcd.: C, 38.91; H, 4.57; N, 18.15%.)

2-(*Trimethylstannyl*)-5-(*p-nitrophenyl*)*tetrazole monohydrate* (*XII*)

An absolute ethanol solution of 0.337 g (1.77 mmole) of trimethyltin hydroxide and 0.321 g (1.78 mmole) of 5-(*p*-nitrophenyl)tetrazole was heated to reflux for 30 min. Evaporation of ethanol gave 0.638 g of yellowish crystals which partially decomposed at 220° with sublimation but did not melt below 280°. NMR (methanol, DSS): singlet 8.23 (4 H), singlet 0.70 (9 H, tin-methyl protons) accompanied by satellite peaks [$J(^{117}Sn–CH_3)$ 67, $J(^{119}Sn–CH_3)$ 71 Hz]. UV: λ_{max} 302 nm, ε_{max} 13,600. IR: 3100–3200 cm^{-1} (broad, water of crystallization), 550 cm^{-1} [ν_{as}(C–Sn–C)], 499 cm^{-1} [too strong to be assigned to ν_s(C–Sn–C)]. (Found: C, 32.28; H, 4.16; N, 18.98. $C_{10}H_{15}N_5O_3Sn$ calcd.: C, 32.29; H, 4.07; N, 18.83%.)

2-(*Trimethylstannyl*)-5-(*p-methoxyphenyl*)*tetrazole* (*XIII*)

An equimolar mixture of 0.312 g (1.77 mmole) of 5-(*p*-methoxyphenyl)tetrazole and 0.322 g (1.78 mmole) of trimethyltin hydroxide in 5 ml of absolute ethanol was heated to reflux for 30 min. Evaporation of ethanol gave 0.598 g (100%) of colourless crystals which were recrystallized from tetrahydrofuran and diisopropyl ether (1/2),

m.p. 210–212° (decomp.). NMR (methanol, DSS): doublet 7.88 (2 H, *ortho*-protons respect to the tetrazole ring), doublet 6.93 (2 H, *meta*-protons), singlet 3.78 (3 H, methoxy protons), singlet 0.68 (9 H, methyl-tin protons) accompanied by satellite peaks [$J(^{117}Sn-CH_3)$ 66, $J(^{119}Sn-CH_3)$ 69 Hz]. UV: λ_{max} 254 nm, ε_{max} 17,900. IR: 542 cm^{-1} [ν_{as}(C–Sn–C)], absence of ν_s(C–Sn–C) at ca. 500 cm^{-1}. (Found: C, 38.90; H, 4.87; N, 16.77. $C_{11}H_{16}N_4OSn$ calcd.: C, 38.98; H, 4.76; N, 16.53%.)

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