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FORMATION OF ORGANOTIN–NITROGEN BONDS

IV*. *N*-TRIALKYLTIN DERIVATIVES OF 4-MONO- OR 4,5-DISUBSTITUTED 1,2,3-TRIAZOLES, 3-PHENYL-1,2,4-TRIAZOLE, 3-PHENYLPYRAZOLE AND 4-PHENYLIMIDAZOLE

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SUMMARY

N-(Trialkylstannyl)-4-mono- or 4,5-disubstituted 1,2,3-triazoles have been prepared by the 1,3-cycloaddition of tri-n-butyltin azide to alkynes and by the condensation of 1,2,3-triazoles with bis(tri-n-butyltin) oxide or trimethyltin hydroxide. The trialkyltin group has been shown to be attached to the 2-nitrogen of the 1,2,3-triazole ring. *N*-Tri-n-butyltin derivatives of 3-phenylpyrazole, 4-phenylimidazole and 3-phenyl-1,2,4-triazole have been prepared by the condensation of bis(tri-n-butyltin)oxide with the corresponding azoles, the tri-n-butyltin group becoming attached to the 1-nitrogen atom of the latter.

INTRODUCTION

N-Trialkyltin and *N*-triphenyltin derivatives of unsubstituted pyrazole, imidazole, 1,2,3-triazole and 1,2,4-triazole have been prepared previously by condensation of the azoles with bis(tri-n-butyltin) oxide, trimethyltin hydroxide, or bis(triphenyltin) oxide[1,2]. A preparation of *N*-(tri-n-butylstannyl)-4,5-bis(ethoxycarbonyl)-1,2,3-triazole by the 1,3-dipolar cycloaddition of tri-n-butyltin azide to diethyl acetylenedicarboxylate has also been described[3]. In the case of these *N*-(organostannyl)-1,2,3-triazoles, the organotin group was said to be attached to the 1-nitrogen atom of the 1,2,3-triazole ring, but no firm evidence was advanced for this[1-3]. Birkofer and Wegner have described the synthesis of 2-trimethylsilyl derivatives of 4-mono- or 4,5-disubstituted 1,2,3-triazoles by the 1,3-cycloaddition of trimethylsilyl azide to alkynes[4].

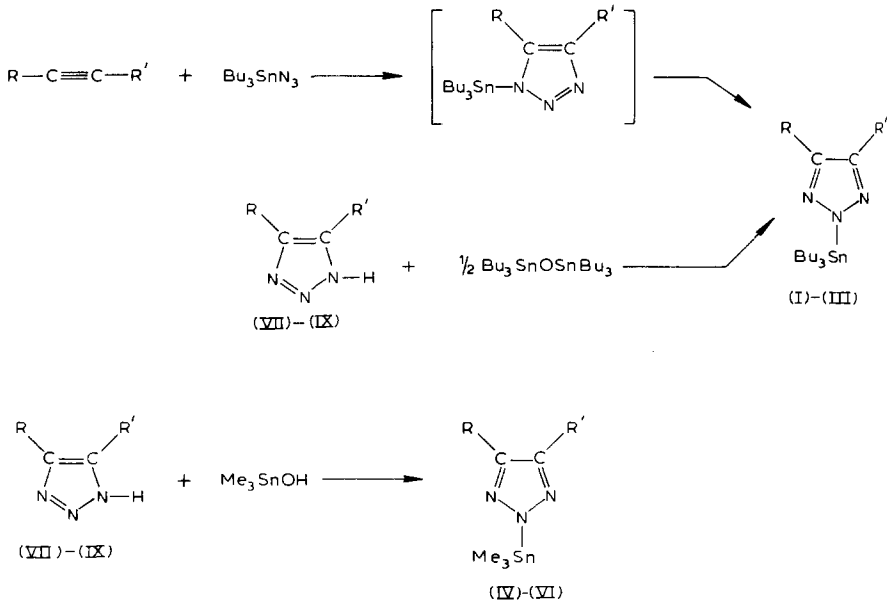
In our previous paper[5] we described the preparation of 2-(trialkylstannyl)-5-substituted tetrazoles by the 1,3-dipolar cycloaddition of trialkyltin azides to nitriles and by the reaction of 5-substituted tetrazoles with bis(tri-n-butyltin) oxide or tri-

* For Part III see ref. 5.

methyltin hydroxide. The NMR and UV spectra and the dipole moments of these products suggested a structure in which the trialkyltin group was attached to the 2-nitrogen atom of the tetrazole ring. In this paper we report the preparation and structural studies of *N*-trialkyltin derivatives of diazoles and triazoles having one or two substituents at the carbon atoms.

RESULTS AND DISCUSSION

N-(Tri-n-butylstannyl)-4-mono- or 4,5-disubstituted 1,2,3-triazoles have been prepared by the 1,3-cycloaddition of tri-n-butyltin azide to alkynes, and also by the condensation of bis(tri-n-butyltin) oxide with the corresponding 1,2,3-triazoles. Both reactions gave a single product, (I)–(III), in which the tri-n-butyltin group is attached to the 2-nitrogen, as shown by the dipole moments, the UV and NMR spectra and also by the viscosity of toluene solutions. Migration of the tri-n-butyltin group from the 1-nitrogen to the 2-nitrogen atom must occur in the cycloaddition, and Birkofer and Wegner described the analogous migration of a trimethylsilyl group in the cycloaddition of trimethylsilyl azide to alkynes[4]. 2-(Trimethyltin) derivatives of the 1,2,3-triazoles, (IV)–(VI), have been obtained quantitatively by the condensation of trimethyltin hydroxide with the 1,2,3-triazoles. However the cycloaddition of trimethyltin azide to alkynes is not a preferred method for the preparation of (IV)–(VI), since trimethyltin azide is partly decomposed under the reaction conditions used (180–200°, 3 days), and is also less reactive toward alkynes than tri-n-butyltin azide.



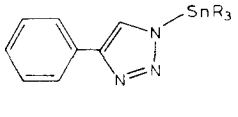
(I), (IV), VII): R, C_2H_5; R′, C_2H_5
(II), (V), (VIII): R, C_6H_5; R′, C_6H_5
(III), (VI), (IX): R, C_6H_5; R′, H

Small dipole moments were reported for 2-trimethylsilyl derivatives of 1,2,3-triazoles[4]; *e.g.*, that of 2-(trimethylsilyl)-4,5-dimethyl-1,2,3-triazole is 0.66 D, and that of the 4-phenyl analogue 1.09 D. Thus, the very small dipole moments of (I) (1.11 D) and (II) (2.94 D) supported a structure in which a tri-n-butyltin group is attached to the 2-nitrogen atom of the 1,2,3-triazole ring.

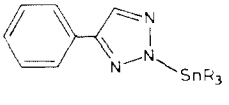
The NMR spectrum of each of the 4,5-diethylderivatives, (I) and (IV), includes a sharp quartet which reveals the presence of two equivalent methylenes of the 4,5-diethyl groups, providing confirmatory evidence for the symmetrical structure in which the trialkyltin group is attached to the 2-nitrogen atom.

The UV spectra of (II) and (V) each showed a larger absorption maximum at the longer wavelength (253 nm, ε_{max} 15,400) than did that of 1-methyl-4,5-diphenyl-1,2,3-triazole (X) (249 nm, ε_{max} 7,600). When the bulky trialkyltin group is attached to the 1-nitrogen, steric interaction may considerably reduce the coplanarity, and hence the delocalization of π-electrons of both the benzene and 1,2,3-triazole rings[5], so that the maximum absorption of (II) and (V) should be rather smaller than that of (X). The NMR spectra of (II) and (V) gave little information on the position of the trialkyltin group, since the multiplet assigned to phenyl protons was too complex.

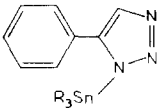
In the case of (III) and (VI), there are three possible structural isomers (A, B and C):



(A)



(B)



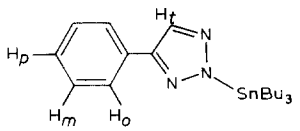
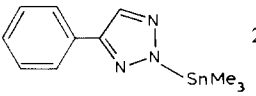
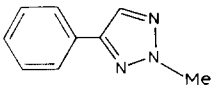
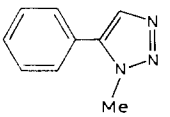
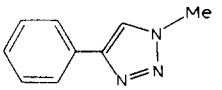
(C)

By comparing the UV and NMR spectra of (III) and (VI) with those of the *N*-methyl analogues (Table 1), structure (C) can be excluded, but it is difficult to decide which of (A) and (B) is the more probable. Even the very low dipole moment of (III) (2.96 D) does not allow a choice to be made. As described below, however, structure (B) is supported for (III) by the measurement of the viscosities of its toluene solutions.

Since a high dependence on concentration was found for the viscosities of toluene solutions of *N*-(tri-n-butyltin) derivatives of imidazole[8], 1,2,4-triazole[8], and 5-substituted tetrazole[5] which have two nitrogens in the 1,3-positions in each ring, it was concluded that these compounds have polymeric structures in toluene. By contrast, there was no such viscosity increase in the case of *N*-(tri-n-butylstannyl)-pyrrole and -pyrazole[8], indicating that they had monomeric structures. We have found that (I)–(III) are monomeric even in concentrated toluene solutions, since little viscosity increase was observed in toluene solutions of (I)–(III) (Fig. 1). This is consistent with the structure in which the tri-n-butyltin group is attached to the 2-nitrogen of the 1,2,3-triazole ring of (I)–(III). If the tri-n-butyltin group were attached to the 1-nitrogen atom, a coordinated polymeric structure would be possible, and a viscosity increase would be expected, since the 1- and 3-nitrogen atoms could be used for the coordination. It is noteworthy that the fact that the trialkyltin group is found to be attached to the 2-nitrogen of the 1,2,3-triazole ring in solutions of (I)–(IV) contrasts with the results for 1-(triphenylstannyl)-1,2,3-triazole[1,2] and 1-(tri-n-butylstannyl)-4,5-bis(ethoxycarbonyl)-1,2,3-triazole[3].

TABLE 1

ULTRAVIOLET AND NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA FOR *N*-SUBSTITUTED-4(OR 5)-PHENYL-1,2,3-TRIAZOLES

Compound	*UV (in EtOH)*		*NMR (in $CDCl_3$) (ppm)*			
	λ_{max} *(nm)*	ε_{max}	$\delta(H_o)$	$\delta(H_{m,p})$	$\delta(H_t)$	$\delta(N\text{-}Me)$
(III) 	248	14,800	7.81	7.33	7.91	
(VI) 	248	14,600	7.73	7.32	7.95	
(XI)[a,b] 	252	16,200	7.74	7.33	7.79	4.22
(XII)[a,c] 	242	11,200	7.47	7.47	7.71	4.08
(XIII)[a,d] 	246	16,800	7.78	7.35	7.71	4.13

[a] Prepared by reaction of (III) with methyl iodide. [b] M.p. 52–54° (lit.[6] m.p. 58°). [c] Liquid (lit.[7] m.p. 38–39°). [d] M.p. 121–122° (lit.[6] m.p. 123°).

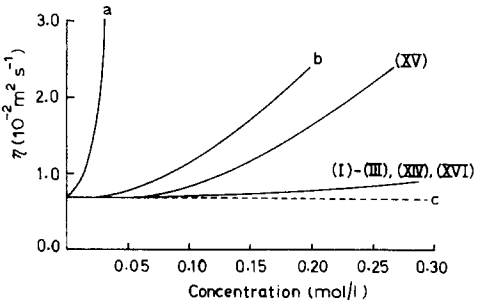
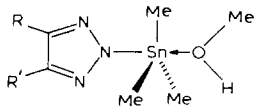
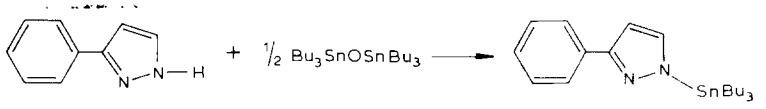


Fig. 1. The viscosities of toluene solutions of *N*-(tri-n-butylstannyl)azoles: *a*, *N*-(tri-n-butylstannyl)imidazole: data from ref. 8: *b*, 2-(tri-n-butylstannyl)-5-phenyltetrazole: data from ref. 5; *c*, pure toluene.

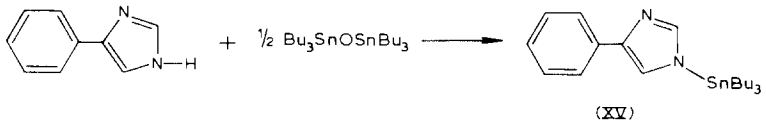
The viscosity and dipole moment of the *N*-(trimethyltin) derivatives (IV)–(VI) were not measured, since these compounds are insoluble in non-polar solvents such as benzene and toluene. Since trimethyltin azide is more polymerised than its higher homologues in the solid state[9], it seems very likely that the *N*-(trimethyltin) derivatives (IV)–(VI) are more polymeric compared with their tri-n-butyltin analogues (I)–(III). This would be consistent with the insolubility of (IV)–(VI) in non-polar solvents, and with the absence of C–Sn–C symmetric stretching vibrations[10] at ca. 500 cm^{-1} in the IR spectra (KBr disc) of (IV)–(VI). In the NMR spectra of (IV)–(VI) in methanol, the coupling constants of the tin–methyl protons, $J(^{117}Sn–CH_3)$ 58, 65 and 63 Hz, respectively, are close to those reported for trimethyltin azide[9,11] and trimethyltin halide[12,13], and smaller than those in *N*-(trimethylstannyl)tetrazoles[5]. The established relationship between the coupling constants of tin–methyl protons and the sp^3d, sp^3d^2 hybridization of tin atom[14] shows that the tin atoms of (IV)–(VI) are penta-coordinated in methanol solutions by coordination with methanol:



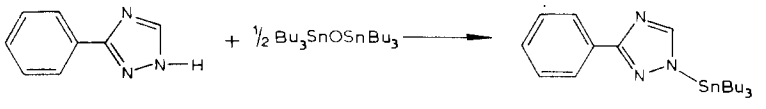
N-(Tri-n-butyltin) derivatives of 3-phenylpyrazole, 4-phenylimidazole and 3-phenyl-1,2,4-triazole were prepared by the condenzation of the corresponding azoles with bis(tri-n-butyltin) oxide, following Van der Kerk's procedure[1–3].



(XIV)



(XV)

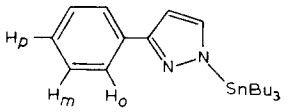
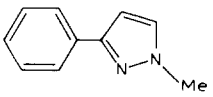
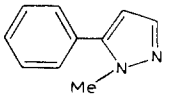
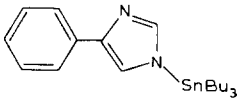
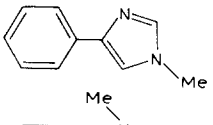
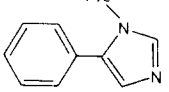
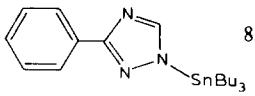


(XVI)

In the NMR spectra of (XIV)–(XVI), the *ortho*-protons on the phenyl group are markedly deshielded compared with the *meta*- and *para*- protons (Table 2). This indicates the co-planarity of the benzene and the azole rings, and thus the tri-n-butyltin group of (XIV)–(XVI) must be attached to the nitrogen atom more remote from the phenyl group. This is supported by a comparison of the chemical shifts for each pair of *N*-methyl isomers of 3-phenylpyrazole and 4-phenylimidazole (Table 2).

TABLE 2

CHEMICAL SHIFTS OF THE PHENYL PROTONS OF *N*-SUBSTITUTED PHENYLDIAZOLES AND PHENYL-1,2,4-TRIAZOLE

Compound	*Chemical shifts (ppm)*[a]		
	$\delta(H_o)$	$\delta(H_{m,p})$	$\delta(H_o)-\delta(H_{m,p})$
(XIV) 	7.83	7.35	0.48
(XVII)[b] 	7.80	7.35	0.45
(XVIII)[b] 	7.39	7.39	0.00
(XV) 	7.79	7.39	0.45
(XIX)[c] 	7.72	7.32	0.40
(XX)[c] 	7.39	7.39	0.00[d]
(XVI) 	8.11	7.38	0.73

[a] Measured in $CDCl_3$ using tetramethylsilane as an internal standard. [b] Prepared by the method of Auwers and Breyham[15]. [c] Prepared by the method of Hajeldine, Pyman and Winchester[16]. [d] The NMR spectrum of 1-ethyl-5-phenylimidazole was reported to have a singlet at δ 7.40 ppm assigned to the five phenyl protons[17].

Little viscosity increase was observed in the case of 1-(tributylstannyl)-3-phenylpyrazole (XIV) and -3-phenyl-1,2,4-triazole (XVI). A small degree of association was found in concentrated toluene solutions of 1-(tri-n-butylstannyl)-4-phenylimidazole (XV) (Fig. 1). It was an unexpected result that the 3-phenyl-1,2,4-triazole derivative (XVI) is not polymeric in toluene, since the unsubstituted 1,2,4-triazole derivative is polymerized to a similar extent as the imidazole one[8]. The variation of this viscosity of solutions of phenylsubstituted isomers, (XV) and (XVI), was far less than that of solutions of *N*-(tri-n-butyltin) derivatives of the unsubstituted imidazole and 1,2,4-triazole[8]. Phenyl substitution apparently leads to a decrease in the viscosity

since an analogous decrease was found in the viscosity of toluene solution of 2-(tri-n-butylstannyl)-5-phenyltetrazole when compared with that of solutions of the 5-alkyl analogues[5].

EXPERIMENTAL

NMR spectra were measured in Cl_3CD at 60 MHz with a Japan Electron Optics C-60HL Spectrometer except that in the case of (V) and (VI) a mixture of deuteriochloroform and methanol was used as solvent. Chemical shifts are given in ppm downfield from internal tetramethylsilane. 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[8]. The results are shown in Fig. 1.

Dipole moment

The dipole moments were determined as previously described[5].

TABLE 3

DIPOLE MOMENT RESULTS

Compound	α	β	$P_{2\infty}$	R_2	μ
(I)	0.78	−0.271	164.3	139.3	1.11
(II)	2.01	−0.315	318.6	142.3	2.93
(III)	1.96	−0.348	301.5	122.2	2.96
(XVI)	2.92	−0.320	342.3	95.4	3.48

2-(*Tri-n-butylstannyl*)-4,5-*diethyl*-1,2,3-*triazole* (*I*)

Method A. A mixture of 10.007 g (0.032 mol) of tri-n-butyltin azide and 5.0 ml of 3-hexyne[18] was heated at 180° for 71 h in a sealed glass bottle until the azide band in the IR spectrum at 2060 cm^{-1} disappeared. After evaporation of surplus 3-hexyne, the reaction mixture was distilled *in vacuo* to give 10.176 g (82%) of (I), b.p. 129–130°/0.6 mmHg, m.p. 41–44°. NMR: quartet δ 2.67 (2H, methylene protons), triplet 1.24 ppm (3H, methyl protons). (Found: C, 52.09; H, 9.06; N, 9.49. $C_{18}H_{37}N_3Sn$ calcd.: C, 52.20; H, 9.00; N, 10.14%.)

An ethereal solution of 1.117 g (0.0027 mol) of (I) was treated with dilute hydrochloric acid. Evaporation of the aqueous layer gave 0.075 g (22%) of 4,5-diethyl-1,2,3-triazole (VII). The ethereal layer was concentrated and the residue dissolved in a small amount of acetone. Addition of ether to the acetone solution gave 0.070 g (16%) of precipitate, which was identified as 4,5-diethyl-1,2,3-triazole hydrogen chloride, m.p. 124° (dec.), Beilstein test for halogen was positive. IR: 1618, 1520, 1357, 1180, 1120, 1068, 1005, 972, 942, 794 cm^{-1}. (Found: C, 44.55; H, 7.52; N, 25.67. $C_6H_{12}N_3Cl$ calcd.: C, 44.58; H, 7.49; N, 26.00%.) The mother liquor was evaporated to dryness, and the residue was dissolved in hot n-hexane. The hexane solution was cooled in a refrigerator to give colourless crystals of (VII), 0.199 g (59%), m.p. 87–89°. IR (nujol): 1602, 1508, 1310, 1248, 1209, 1120, 1060, 1014, 967, 787 cm^{-1}. Mass spectrum: 125 (M^+, 74), 124 (19), 110 (100), 96 (19), 82 (32). NMR: quartet δ 2.70 (2H,

methylene protons), triplet 1.27 (3H, methyl protons), singlet 13.00 ppm (1H, N–H). (Found: C, 58.27; H, 9.15; N, 33.83. $C_6H_{11}N_3$ calcd.: C, 57.57; H, 8.86; N, 33.58%.)

Method B. A mixture of 0.019 g (0.15 mmol) of (VII) and 0.045 g (0.075 mmol) of bis(tri-n-butyltin) oxide in benzene was heated to reflux under 3 h. After evaporation of benzene, the product was distilled to give 0.063 g (100%) of crystals, which were identified as (I) from their IR and NMR spectra.

2-(*Tri-n-butylstannyl*)-4,5-*diphenyl*-1,2,3-*triazole* (*II*)

Method A. A mixture of 13.415 g (0.0405 mol) of tri-n-butyltin azide with 7.0 g of diphenylacetylene was heated at 150° for 70 h. Removal of residual diphenylacetylene by vacuum distillation gave crystals which were recrystallized from n-hexane to give 17.781 g (86%) of (II), m.p. 65–66°. UV: λ_{max} 253 nm, ε_{max} 15,400. NMR: multiplet δ 7.09–7.65 ppm (phenyl protons). (Found: C, 61.49; H, 7.54; N, 8.41. $C_{26}H_{37}N_3Sn$ calcd.: C, 61.20; H, 7.25; N, 8.24%.)

An ethereal solution of 0.678 g of (II) was treated with hydrochloric acid to give 4,5-diphenyl-1,2,3-triazole (VIII). The mixture was made basic with aqueous sodium hydroxide. The lower aqueous layer was separated, acidified with dilute hydrochloric acid, and kept in a refrigerator to yield 0.234 g (80%) of crystalline (VIII), m.p. 139–140° (lit.[19] 138°). Mass spectrum: 222 (19), 221 (M^+, 100), 220 (16), 193 (12), 165 (36), 118 (11), 91 (15).

Method B. A mixture of 0.080 g (0.362 mmol) of (VIII) and 0.108 g (0.181 mmol) of bis(tri-n-butyltin) oxide in benzene was heated under reflux for 3 h. Removal of benzene *in vacuo* gave (II) as a pasty liquid, which crystallized on standing at room temperature. The IR, UV and NMR spectra were superimposable on those of (II) obtained by the cycloaddition.

2-(*Tri-n-butylstannyl*)-4-*phenyl*-1,2,3-*triazole* (*III*)

Method A. On heating 8.713 g (0.0363 mol) of tri-n-butyltin azide in 5.0 ml of phenylacetylene at 140° for 12 h, the azide was completely consumed. Residual phenylacetylene was evaporated off to give 12.50 g of pasty crystals, which were recrystallized from acetonitrile to yield 6.958 g (61%) of (III), m.p. 90–91°. UV: λ_{max} 248 nm, ε_{max} 14,800. NMR: doublet δ 7.81 (2H, *ortho*-protons), multiplet 7.33 (3H, *meta* and *para*-protons), singlet 7.91 ppm (1H, 5-proton). (Found: C, 54.85; H, 7.89; N, 9.48. $C_{20}H_{33}N_3Sn$ calcd.: C, 55.30; H, 7.60; N, 9.68%.)

Treatment of (III) with hydrochloric acid by the analogous procedure to the case of (II) afforded 0.255 g (75%) of 4-phenyl-1,2,3-triazole (IX), m.p. 148–150° (lit.[20] 148.4°). The UV and IR spectra were superimposable on those of an authentic sample[20] of (IX). UV: λ_{max} 248 nm, ε_{max} 14,800. NMR (in MeOH and $CDCl_3$ with TMS): multiplet δ 7.80 (2H, *ortho*-protons), multiplet 7.40 (3H, *meta* and *para*-protons), singlet 8.12 ppm (1H, 5-proton). Mass spectrum: 145 (M^+, 100), 118 (18), 91 (21), 77 (14), 63 (14), 51 (13).

Method B. A benzene solution of 0.0363 g (0.251 mmol) of (IX) and 0.0747 g (0.125 mmol) of bis(tri-n-butyltin) oxide was heated to reflux for 3 h. Distillation of benzene *in vacuo* gave pasty crystals, the spectra of which were superimposable on those of (III) prepared by the cycloaddition.

2-(*Trimethylstannyl*)-4,5-*diethyl*-1,2,3-*triazole* (*IV*) *and its monohydrate*

An equimolar mixture of 0.032 g (0.026 mmol) of (VII) with 0.047 g (0.026

mmol) of trimethyltin hydroxide[21] in dry benzene was heated under reflux for 30 min. Benzene was distilled off to give 0.075 g of colorless crystals (IV), m.p. 125–126° (with sublimation). IR (KBr disc); there was no broad band at 917 cm^{-1} assigned to Sn–O–H[22] of trimethyltin hydroxide, 1557, 1549, 1190, 1157, 1056, 976, 960, 780, 643, 628, 546 cm^{-1}. NMR (in MeOH and $CDCl_3$): quartet δ 2.66 (2H, methylene protons), triplet 1.23 (3H, methyl protons), singlet 0.61 ppm (9H, tin–methyl protons) accompanied by small satellite peaks [$J(^{117}Sn–CH_3)$ 58, $J(^{119}Sn–CH_3)$ 60 Hz]. (Found: C, 37.49; H, 6.85; N, 14.71. $C_9H_{19}N_3Sn$ calcd.: C, 37.28; H, 6.61; N, 14.49%.)

On exposure of (IV) to moist air, fine long needles began to grow from it after several days. One month later, (IV) was completely converted into the long needles, the IR spectrum of which [3200, 1524, 1200, 1177, 1157, 1056, 980, 960, 785, 680 cm^{-1}, different from that of the original (IV)] showed the presence of water of crystallization at 3200 cm^{-1}. Under vacuum the needles liberated water of crystallization to regenerate (IV).

2-(*Trimethylstannyl*)-4,5-*diphenyl*-1,2,3-*triazole* (*V*)

Analogous treatment of (VIII) and trimethyltin hydroxide gave (V) quantitatively, m.p. 208–210° (cyclohexane/benzene). IR (KBr disc): 1238, 1180, 1172, 1165, 1090, 1070, 1017, 1004, 988, 910, 776, 765, 732, 696, 680, 666 cm^{-1}. NMR (in MeOH and $CDCl_3$): multiplet δ 7.38 (5H, phenyl protons), singlet 0.54 ppm (9H, tin–methyl protons) with satellite peaks [$J(^{117}Sn–CH_3)$ 65, $J(^{119}Sn–CH_3)$ 68 Hz]. UV: λ_{max} 254 nm, ε_{max} 15,400. (Found: C, 53.29; H, 5.29; N, 10.94. $C_{17}H_{19}N_3Sn$ calcd.: C, 53.16; H, 4.99; N, 10.94%.)

2-(*Trimethylstannyl*)-4-*phenyl*-1,2,3-*triazole* (*VI*)

Analogous treatment of (IX) with trimethyltin hydroxide gave (VI), m.p. 191–193°. IR (KBr disc): 1353, 1238, 1182, 1140, 1120, 1081, 1000, 977, 912, 837, 784, 764, 697, 686 cm^{-1}. NMR (in MeOH and $CDCl_3$): multiplet δ 7.73 (2H, *ortho*-protons), multiplet 7.32 (3H, *meta*-, *para*-protons), singlet 7.95 (1H, 5-proton), singlet 0.56 ppm (9H, tin–methyl protons) with satellite peaks [$J(^{117}Sn–CH_3)$ 63, $J(^{119}Sn–CH_3)$ 65 Hz]. UV: λ_{max} 248 nm, ε_{max} 14,600. (Found: C, 42.58; H, 5.16; N, 13.27. $C_{11}H_{15}N_3Sn$ calcd.: C, 42.90; H, 4.91; N, 13.65%.)

1-(*Tri-n-butylstannyl*)-3-*phenylpyrazole* (*XIV*)

A mixture of 4.50 g (31.2 mmol) of 3-phenylpyrazole and 8.70 g (14.7 mmol) of bis(tri-n-butyltin) oxide dissolved in benzene was heated under reflux for 48 h under nitrogen. Water formed by the condensation was removed as an azeotropic mixture with benzene using Soxhlet extractor containing Drierite. Evaporation of benzene *in vacuo* to dryness gave an oil, which was distilled under nitrogen, b.p. 206.5–208°/2.5 mmHg, n_D^{25} 1.5447, 8.85 g (70%). The product underwent hydrolysis on exposure to moist air, the characteristic IR bands of the product at 1490, 1120, 1038 cm^{-1} disappearing after exposure for 3 min. Bands characteristic of the starting 3-phenylpyrazole at 1200, 955 cm^{-1} were absent from the IR spectrum of (XIV). Nitrogen analysis was carried out by titration with hydrochloric acid[23]. (Found: N, 6.56. $C_{21}H_{34}N_2Sn$ calcd.: N, 6.65%.)

1-(*Tri-n-butylstannyl*)-4-*phenylimidazole* (*XV*)

Treatment of 1.50 g (10.4 mmol) of 4-phenylimidazole with 3.10 g (5.20 mmol)

of bis(tri-n-butyltin) oxide under nitrogen gave a pasty oil in a quantitative yield, b.p. 193°/0.03 mmHg, n_D^{25} 1.5625. IR: 2650, 1120, 1020, 860 cm^{-1}. The band at 2650 cm^{-1} disappeared on exposure to air for 4 min. (Found: N, 6.89[23]. $C_{21}H_{34}N_2Sn$ calcd.: N, 6.65%.)

1-(*Tri-n-butylstannyl*)-3-*phenyl*-1,2,4-*triazole* (*XVI*)

A mixture of 0.241 g (1.66 mmol) of 3-phenyl-1,2,4-triazole[24] and 0.496 g (0.833 mmol) of bis(tri-n-butyltin) oxide in 10 ml of benzene was heated under reflux for 30 min. Removal of benzene *in vacuo* gave 0.724 g (100%) of a pasty liquid of (XVI) which crystallized on standing in a refrigerator for several days, m.p. 48–51°. NMR: multiplet δ 8.11 (3H, 5-proton and *ortho*-protons), multiplet 7.38 (3H, *meta* and *para*-protons), multiplet 0.7–1.7 ppm (27H, n-butyl protons). UV: λ_{max} 244 nm ε_{max} 14,000. (Found: C, 54.99; H, 7.63; N, 9.53. $C_{20}H_{33}N_3Sn$ calcd.: C, 55.33; H, 7.66; N, 9.68%.)

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