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# FORMATION OF ORGANOTIN-NITROGEN BONDS

## VII. STRUCTURAL STUDIES OF 2-(TRIALKYLSTANNYL)-4,5-BIS(ALKOXYCARBONYL)-1,2,3-TRIAZOLES BY $^{13}$C-NMR SPECTROSCOPY

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## SUMMARY

The structure of N-(trialkylstannyl)-4,5-bis(alkoxycarbonyl)-1,2,3-triazoles has been studied by $^{13}$C-NMR spectroscopy. The trialkylstannyl group has been found to be attached to the 2-nitrogen atom of the 1,2,3-triazole ring.

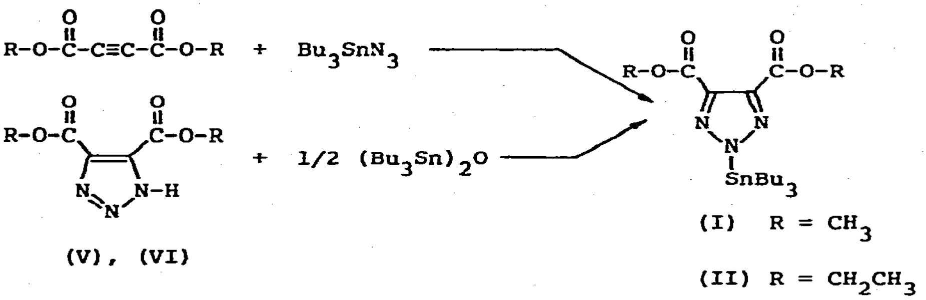
## INTRODUCTION

Luijten and van der Kerk prepared N-(tributylstannyl)-4,5-bis(ethoxycarbonyl)-1,2,3-triazole in which the tributylstannyl group was said to be attached to the 1-nitrogen atom of the 1,2,3-triazole ring, but no structural information was presented [1]. In our previous paper, the $^{1}$H-NMR and UV spectra and dipole moments of N-(trialkylstannyl)-4-mono- or 4,5-disubstituted 1,2,3-triazoles showed that the N-trialkylstannyl group was attached to the 2-nitrogen atom [2].

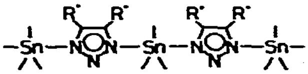
Structural studies of N-(trialkylstannyl)-4,5-bis(alkoxycarbonyl)-1,2,3-triazoles have been carried out by measuring their $^{13}$C-NMR spectra. In these compounds, the $^{1}$H-NMR and UV spectra did not afford useful information on the position of the N-trialkylstannyl group.

## RESULTS AND DISCUSSIONS

N-(Tributylstannyl)-4,5-bis(methoxycarbonyl)- and 4,5-bis(ethoxycarbonyl)-1,2,3-triazoles, (I) and (II), were prepared by 1,3-dipolar cycloaddition of tributyltin azide to dialkyl acetylenedicarboxylates and by the condensation of bis(tributyltin) oxide with free 4,5-bis(alkoxycarbonyl)-1,2,3-triazoles. Both reactions afforded a single product. The $^{13}$C-NMR spectrum of (I) measured at room temperature showed a single peak at 139.7 ppm assigned to the 4- and 5-carbon atoms of the 1,2,3-triazole ring (Table 1). In addition, the two carbonyl carbons also displayed a single peak at 161.9 ppm. Since these results show both the equivalencies of the 4- and 5-carbons and of the two carbonyl carbons, compound (I) should have a symmetrical structure. Thus, the tributylstannyl group has been suggested to be attached to the 2-nitrogen atom of the 1,2,3-triazole ring.



Measurements of the molecular weights of compounds (I) and (II) have shown a monomeric structure in chloroform solution, accordingly, the $^{13}$C-NMR spectra have been measured in monomeric state. This result excludes the possibility that the equivalency of the 4- and 5-carbon atoms was caused by the intermolecular associated structure in which the 1- and 3-nitrogen atoms are coordinated to tin atoms as shown below:



There is another possible explanation for the observation that the 4- and 5-carbon atoms exhibit a single peak in the $^{13}C$-NMR spectrum: Quicker intramolecular transposition of tributylstannyl group among the nitrogen atoms than the time scale of NMR spectrometer could cause a single peak [3]. Since the low temperature $^{13}C$-NMR spectrum, measured at -50°, displayed a single peak at 137.7 ppm assigned to the equivalent 4- and 5-carbon atoms (Table 1), the possibility of the quick transposition might be less. But, this explanation could not be eliminated completely, if this type of transposition is considerably fast even at -50°.

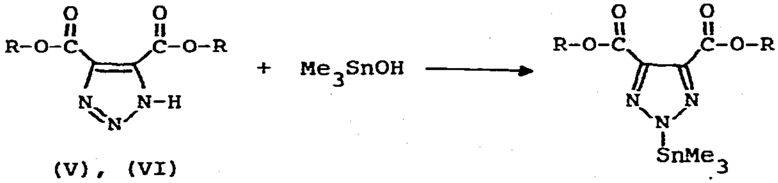
In the $^{13}C$-NMR spectra of 2-(tributylstannyl)-4,5-bis(ethoxycarbonyl)-, -4,5-diethyl-, and 4,5-diphenyl-1,2,3-triazole (II, III, and IV), the 4- and 5-carbon atoms signals were seen as a single paek both at room temperature and at -50° (Table 1). These results also support the symmetrical structure of II, III and IV, in which the tributylstannyl group is attached to the 2-nitrogen atom.

2-(Trimethylstannyl)-4,5-bis(methoxycarbonyl)- and -4,5-bis(ethoxycarbonyl)-1,2,3-triazoles (VII and VIII) have been prepared in quantitative yield by the condensation of trimethyltin hydroxide with the free 1,2,3-triazoles. The $^{13}C$-NMR spectra, measured in acetone-$d_6$ at room temperature and at -50°, also have exhibited the equivalency of the 4- and 5-carbon atoms (Table 1). Since the molecular weights of VII and VIII have been found to be monomeric in acetone, the trimethylstannyl group must be attached to the 2-nitrogen atom of the 1,2,3-triazole ring.

TABLE 1

$^{13}$C-NMR SPECTRAL DATA FOR THE 1,2,3-TRIAZOLES

| Compd. No. | 4,5-Substituent | Temperature | Chemical shifts of carbon atoms (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 4,5-Substituent | | | | Butyl- and methyltin group | | | |
| | | | 4,5- | carbonyl | methyl | methylene | α | β | γ | δ |
| (I) | COOCH$_3$ | room temp. | 139.7 | 161.9 | 52.5 | --- | 16.6 | 27.9 | 27.0 | 13.6 |
| (I) | COOCH$_3$ | -50° | 137.7 | 161.5 | 52.8 | --- | 18.4 | 28.2 | 27.0 | 13.8 |
| (II) | COOC$_2$H$_5$ | room temp. | 139.5 | 161.7 | 14.1 | 61.6 | 16.5 | 27.8 | 27.0 | 13.6 |
| (II) | COOC$_2$H$_5$ | -50° | 139.3 | 161.8 | 14.2 | 61.7 | 16.8 | 27.9 | 27.1 | 13.6 |
| (III) | C$_2$H$_5$ | room temp. | 146.4 | --- | 14.2 | 18.3 | 15.3 | 28.0 | 27.0 | 13.6 |
| (III) | C$_2$H$_5$ | -50° | 145.8 | --- | 14.7 | 18.1 | 15.6 | 28.0 | 27.3 | 13.9 |
| (IV) | C$_6$H$_5$ | room temp. | 144.6 | --- | --- | --- | 15.4 | 27.9 | 26.9 | 13.6 |
| (IV) | C$_6$H$_5$ | -50° | 144.4 | --- | --- | --- | 15.5 | 27.9 | 27.2 | 13.9 |
| (V) | COOCH$_3$ | room temp. | 138.6 | 160.5 | 53.2 | --- | --- | --- | --- | --- |
| (VI) | COOC$_2$H$_5$ | room temp. | 138.5 | 160.2 | 14.1 | 62.5 | --- | --- | --- | --- |
| (VII) | COOCH$_3$ | room temp. | 139.0 | 162.6 | 51.5 | --- | -1.7 | --- | --- | --- |
| (VII) | COOCH$_3$ | -50° | 138.7 | 162.5 | 51.5 | --- | -2.0 | --- | --- | --- |
| (VIII) | COOC$_2$H$_5$ | room temp. | 139.2 | 162.3 | 13.9 | 61.0 | -1.5 | --- | --- | --- |
| (VIII) | COOC$_2$H$_5$ | -50° | 138.5 | 161.9 | 13.6 | 61.0 | -1.5 | --- | --- | --- |



(V), (VI)

(VII) R = $CH_3$

(VIII) R = $CH_2CH_3$

EXPERIMENTAL

$^{13}$C-NMR spectra were recorded in the pulse Fourier transform mode with a JEOL-FX60 spectrometer operating at a resonance frequency of 15.03 MHz. The parameters used were: pulse width 8 μsec, spectral width 5000Hz for 8K data points. Molecular weights were measured at 30.0° in chloroform and acetone solution by the vapor pressure equilibrium technique [4].

2-(Tributylstannyl)-4,5-diethyl- and -4,5-diphenyl-1,2,3-triazoles (III and IV) wer prepared as described previously [2]. 4,5-Bis(methoxycarbonyl)-1,2,3-triazole (V) was prepared by the reaction of dimethyl acetylenedicarboxylate with sodium azide according to the method of Tanaka, Velen and Miller [5].

Preparation of 4,5-bis(ethoxycarbonyl)-1,2,3-triazole (VI)

The triazole (VI) also was prepared by the analogous procedure from diethyl acetylenedicarboxylate and sodium azide according to the method of Tanaka, Velen and Miller [5]. The triazole (VI) was a liquid purified by elution chromatography (Silica gel, ether), $n_D^{25}$ 1.4861. $^1$H-NMR ($CDCl_3$): 1.40 (t, $CH_3$, J 7.2 Hz), 4.49 (q, $CH_2$), 13.0 ppm(N-H). IR (nujol) 3200 (N-H), 1735 cm$^{-1}$(C=O). (Found: C, 44.90; H, 5.46; N, 19.43. $C_8H_{11}N_3O_4$ calcd.: C, 45.07; H, 5.20; N, 19.71%)

## Preparation of 2-(tributylstannyl)-4,5-bis(methoxycarbonyl)-1,2,3-triazole (I)

(A) A mixture of 0.944 g (5.10 mmol) of 4,5-bis(methoxycarbonyl)-1,2,3-triazole (V), mp 132°, and 1.520 g (2.55 mmol) of bis(tributyltin) oxide in 30 ml of ethanol was heated to reflux for 30 min. Removal of ethanol *in vacuo* gave 2.418 g (100%) of pure crystals, mp 98-99°. $^1$H-NMR ($CDCl_3$): 3.96 ppm ($CH_3$). Molecular weight ($CHCl_3$): Found, 473 (0.015 M/kg); calcd., 474.17. (Found: C, 45.85; H, 7.11; N, 8.82. $C_{18}H_{33}N_3O_4Sn$ calcd.: C, 45.60; H, 7.02; N, 8.86%)

(B) A mixture of 1.425 g (10.03 mmol) of dimethyl acetylenedicarboxylate and 3.331 g (10.03 mmol) of tributyltin azide in 60 ml of benzene was heated to reflux for 2.5 hr. Removal of benzene by distillation gave 4.618 g (97.1%) of pale yellow pasty liquid. The $^1$H-NMR, $^{13}$C-NMR, and IR spectra of this product were superimpossoble on those of the product obtained by the condensation method (A).

## Preparation of 2-(tributylstannyl)-4,5-bis(ethoxycarbonyl)-1,2,3-triazole (II)

(A) A mixture of 0.610 g (2.86 mmol) of 4,5-bis(ethoxycarbonyl)-1,2,3-triazole and 0.852 g (1.43 mmol) of bis(tributyltin) oxide in 30 ml of ethanol was heated to reflux for 30 min. Removal of ethanol *in vacuo* gave 1.436 g (100%) of II, colorless crystals, mp 79-80° (*lit.*[1], 64.5-67°). $^1$H-NMR ($CDCl_3$): 1.40 (t, $CH_3$, J 7.2Hz), 4.41 ppm (q, $CH_2$-O). Molecular weight ($CHCl_3$): Found, 493 (0.015 M/kg); calcd., 502.22. (Found: C, 48.01; H, 7.56; N, 8.37. $C_{20}H_{37}N_3O_4Sn$ calcd.: C, 47.83; H, 7.43; N, 8.37%)

(B) Compound (II) was prepared by 1,3-dipolar cycloaddition of diethyl acetylenedicarboxylate to tributyltin azide according to the method of Luijten and van der Kerk [1]. The product was a pale brownish pasty liquid which did not crystallize. However, the $^{1}$H-NMR, $^{13}$C-NMR, and IR spectra of this product were superimpossoble on those of the product obtained by the condensation method (A).

### Preparation of 2-(trimethylstannyl)-4,5-bis(methoxycarbonyl)-1,2,3-triazole (VII)

A mixture of 0.206 g (1.11 mmol) of 4,5-bis(methoxycarbonyl)-1,2,3-triazole (V) and 0.201 g (1.11 mmol) of trimethyltin hydroxide in 20 ml of ethanol was heated to reflux for 30 min. Removal of ethanol in vacuo gave 0.385 g (99.7%) of colorless crystalline VII, mp 169-171°. $^{1}$H-NMR (acetone-$d_6$): 0.73 ($CH_3$-Sn, J($^{119}$Sn-$CH_3$) 70.0 Hz), 3.89 ppm ($CH_3$-O). Molecular weight (acetone): Found, 355 (0.035 M/kg), 348 (0.010 M/kg); calcd., 347.93. (Found: C, 31.19; H, 4.29; N, 12.20. $C_9H_{15}N_3O_4Sn$ calcd.: C, 31.07; H, 4.35; N, 12.08%)

### Preparation of 2-(trimethylstannyl)-4,5-bis(ethoxycarbonyl)-1,2,3-triazole (VIII)

This compound (VIII) was prepared in quantitative yield by the condensation method as described above, mp 153-155°. $^{1}$H-NMR (acetone-$d_6$): 0.75 ($CH_3$-Sn, J($^{119}$Sn-$CH_3$) 70.4 Hz), 1.37 (t, $CH_3$ of ethyl group), 4.35 ppm (q, $CH_2$). Molecular weight (acetone): Found, 384 (0.035 M/kg), 381 (0.010 M/kg); calcd., 375.98. (Found: C, 35.37; H, 4.98; N, 11.26. $C_{11}H_{19}N_3O_4Sn$ calcd.: C, 35.14; H, 5.09; N, 11.18%)

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