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GROUP IVB ORGANOMETALLIC DERIVATIVES: SYNTHESIS AND ^{13}C NMR SPECTRA OF NEW SILYL AND STANNYL ISOXAZOLES

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Summary

Several new organometallic isoxazoles, silylated and stannylated in the heterocyclic ring or in a side chain have been made. Their ^{13}C NMR spectra are consistent with the previous conclusions on the electronic effects of MR_3 and CH_2MR_3 (M = Si, Sn) groups, and indicate the importance of the p_π-d_π and σ-π mechanisms in the various ring positions.

Introduction

The synthesis of silylated and stannylated heterocycles has developed rapidly in recent years, partly because of the synthetic potential of this type of compound [1]. Although furan, thiophene and pyridine derivatives are known with SiR_3 and/or SnR_3 groups bonded to the nuclear carbon atoms [2], or in the side chain [3], and there have been a few reports of the synthesis and properties of silylated and stannylated five-membered heterocycles containing two or more heteroatoms [4a—c]. The general procedure for forming C—M (M = Si, Sn) bonds to the heteroaromatic systems is coupling of L_3MCl with appropriate organolithium derivatives (produced by hydrogen—lithium or halogen—lithium exchange or organomagnesium compounds. Two step addition reactions [4b] and 1,3 dipolar cycloadditions [4c] to acetylenic type systems have also been employed recently in the synthesis of silyl-isoxazoles, -pyrazoles, and -triazoles. All the above methods have some limitations, in particular, the dipolar additions while giving good yields, are very dependent on the nature of the dipolarophile.

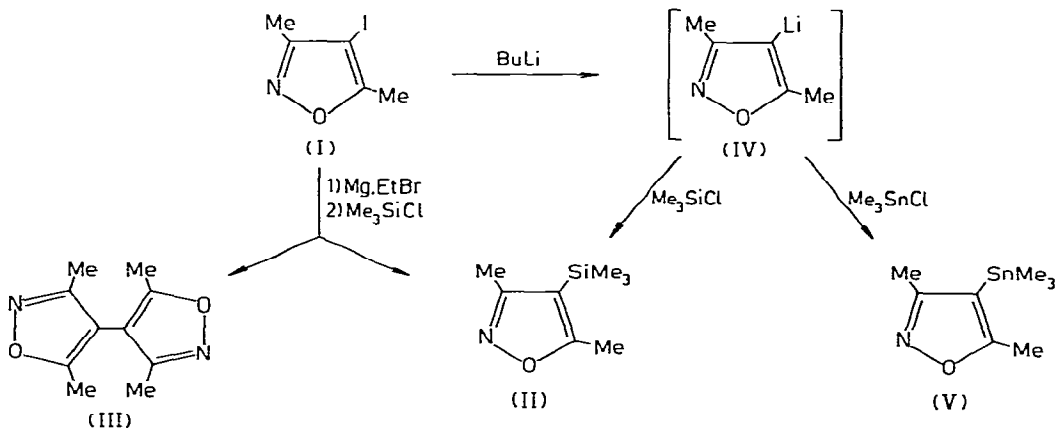
In this paper the preparations of some new silyl and stannyl isoxazoles are reported, and the electronic effect of the MR_3 groups in the various ring positions is investigated through their ^{13}C NMR spectra.

Results and discussion

Heteroaromatic reactions

Silylation and stannylation at the 4-position of the isoxazole ring were achieved by use of 4-iodo-3,5-dimethylisoxazole (I) as starting material. When the corresponding isoxazolylmagnesium iodide, prepared in dry ether [5] with ethyl bromide as "entrainer", was treated with Me_3SiCl, 3,5-dimethyl-4-(trimethylsilyl)-isoxazole (II) was obtained in 27% yield. The poor yield was to some extent attributable to a side reaction giving rise to a sizeable amount of tetramethyl-4,4'-diisoxazole (III). More satisfactory results were achieved by using lithium—halogen exchange; treatment of 3,5-dimethyl-4-lithioisoxazole (IV), obtained from I and n-BuLi, with Me_3SiCl and Me_3SnCl, gave the isoxazole derivatives II and V in 72 and 69% yields, respectively (Scheme 1)

SCHEME 1



In contrast with these relatively simple reactions, nuclear silylation at the position 5 proved to be much more difficult. Although both trimethylsilyl and bistrimethylsilylacetylene react readily with acetonitrile oxide to give 3-methyl-5-(trimethylsilyl)- and 3-methyl-4,5-bis(trimethylsilyl)isoxazole, respectively, in good yields [4a—c], no silylisoxazole was obtained when trimethylsilylpropyne was treated with the same reagent, probably owing to the low reactivity of this acetylenic silicon derivative in the cycloaddition reactions [4c]. In fact even when it was allowed to react with benzonitrile oxide at room temperature, the only cyclic product, which was isolated in quantitative yields, was diphenylfuroxan.

Several attempts to obtain 3,4-dimethyl-5-(trimethylsilyl)isoxazole by treatment of 3,4-dimethylisoxazole with n-BuLi or MeLi and Me_3SiCl gave unsatisfactory results because of the very low stability of the intermediate 5-lithioisoxazole [6]. The predominant products came from ring cleavage, a small

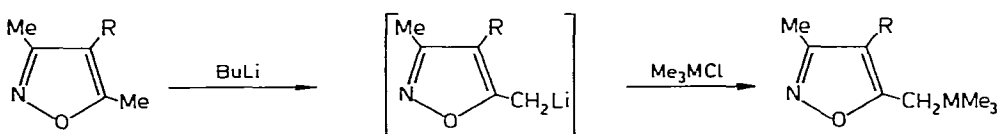
amount of the expected silyl derivative was detected by GLC-MS analysis, but no attempt was made to isolate it.

Side-chain reactions

In the hydrogen—lithium exchange reactions, it is generally accepted that the principal factors which determine the site of the lithiation in the heterocyclic compounds are the acidities of the hydrogens, which depend mainly on the inductive effects in the ring, and coordination of the lithiating agent to the endo- or exocyclic heteroatoms [7]. Thus according to Micetich [8], 3,5-dimethylisoxazole (VI), reacted with n-BuLi to give specific metallation at the C-5 methyl group; treatment of the crude 3-methyl-5-(lithiomethyl)isoxazole with Me_3SiCl gave 3-methyl-5-(trimethylsilylmethyl)isoxazole (VIII) in 70% yield.

Regioselective metallation at the same position was also found for the previously unexplored trimethylisoxazole VII; the corresponding 5-lithiomethyl derivative, obtained from VII and n-BuLi in dry THF, reacted with Me_3SiCl and Me_3SnCl to give compounds IX and X, respectively, in high yields; when the same reactions were carried out in ether, the yields were appreciably lower (Scheme 2).

SCHEME 2

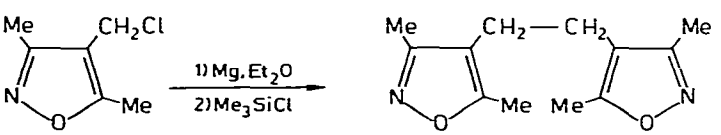


(VI) R=H
(VII) R=Me

(VIII) R=H, M=Si
(IX) R=Me, M=Si
(X) R=Me, M=Sn

Side-chain silylation and stannylation at the C-3 and C-4 methyl groups were less straightforward. The hydrogen—lithium exchange is unsuitable because of the lower acidity of these protons as compared with those of the methyl group at the 5-position. Instead, an organomagnesium-based procedure was used, starting from 3,5-dimethyl-4-(chloromethyl)- (XI) and 5-methyl-3(chloromethyl)isoxazole (XII). When these compounds were used in a normal Grignard synthesis, only small amounts of silylated products were obtained. For instance, treatment of compound XI with Mg turnings in dry ether, followed by Me_3SiCl, gave 1,2-bis(3,5-dimethylisoxazol-4-yl)ethane (XIII), along with traces of 3,5-dimethyl-4-(trimethylsilylmethyl)isoxazole (XIV) which was identified by GLC-MS analysis (Scheme 3).

SCHEME 3

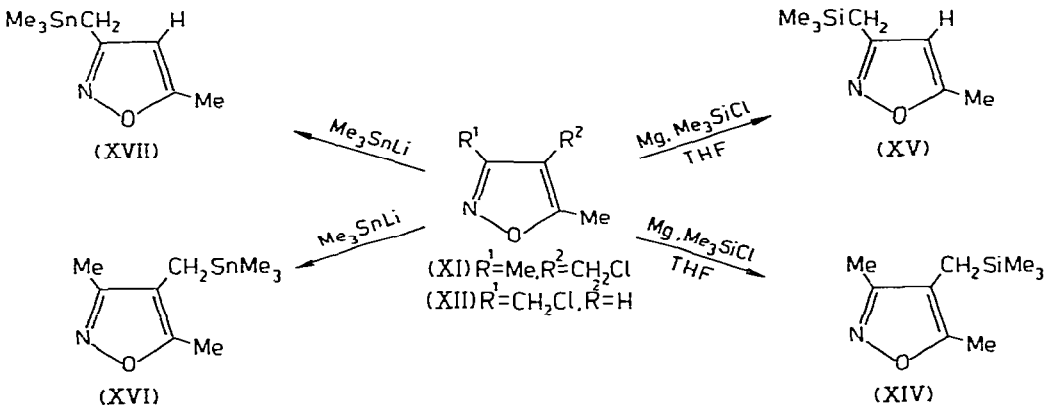


(XI)

(XIII)

Halides XI and XII did, however, satisfactorily undergo in situ reactions in THF containing Me_3SiCl as cosolvent. In this manner the silyl derivatives XIV and XV were obtained in good yields. Unfortunately this procedure could not be used for the synthesis of the corresponding tin derivatives because of predominant side-reaction between Mg and Me_3SnCl. The desired products XVI and XVII were thus prepared by an alternative procedure based on the reaction of the chloromethyl derivatives XI and XII with lithium trimethyltin, according to Scheme 4.

SCHEME 4



The structures of all the new compounds were confirmed by analytical and spectrometric data (see Experimental).

^{13}C NMR spectra

Since the nature of the interaction of C—M bonds (M = Si, Ge, Sn and Pb) with π electron systems continues to be of interest [9], we used ^{13}C chemical shifts as a probe for the electronic substituent effects of the MR_3 and CH_2MR_3 (M = Si, Sn) groups on the isoxazole ring. The basic assumption in using substituent-induced changes in ^{13}C chemical shifts to monitor electronic effects is that these parameters reflect changes in ground state electron density.

The ^{13}C chemical shifts for the silicon- and tin-containing isoxazoles are listed in Table 1; the assignment of the signals of the ring carbon atoms, was made by use of the chemical shift values previously reported for various model compounds [10]. As shown in Table 1, the chemical shifts of the heteroaromatic carbon atoms depend appreciably on both the nature and the position of the substituents. In line with the behaviour of other aromatic and heterocyclic systems, compounds II and V exhibit, compared with to 3,5-dimethylisoxazole (VI), a downfield shift (4.4 and 3.2 ppm respectively) for the C-4 carbon atom bound directly to the metal; these effects of Me_3Si and Me_3Sn groups on the substituted carbon are, however, consistently lower than those reported for the corresponding benzene and pyridine trialkylmetal derivatives *. Similarly the C-3 and C-5

* A low-field shift of 13.2 ppm in respect to benzene, has been observed [11] for the substituted carbon atom in $C_6H_5MR_3$ series (M = Si, Sn); in trialkylmetal derivatives of pyridine, on the other hand, this low-field shift lies in the range 8.3—17.6 ppm for Me_3Si and 12.2—22.5 ppm for Me_3Sn, according to the substitution pattern [12].

TABLE 1

^{13}C NMR CHEMICAL SHIFTS OF SUBSTITUTED ISOXAZOLES [a]

Compound	Signals of ring carbon atoms		
	C-3	C-4	C-5
II	163.3	106.9	173.5
III	159.7	105.0	167.6
V	164.0	105.7	173.2
VI	159.8	102.5	169.2
VII	159.7	109.0	164.2
VIII	159.8	100.1	172.0
IX	159.7	106.4	167.4
XIII	159.3	112.2	165.4
XIV	158.9	110.9	162.1
XV	161.9	101.8	168.4
XVI	158.6	113.5	160.9
XVII	164.2	101.3	168.4

[a] In $CDCl_3$, downfield from internal tetramethylsilane.

resonances were shifted downfield by 3.5 and 4.3 ppm in II and 4.2 and 4.0 ppm in V when compared with the ^{13}C chemical shifts at C-3 and C-5 in VI. The usual assumption that in aromatic and heterocyclic Group IVB organometallic derivatives there is a considerable interaction between the π ring and metal d orbitals [13], can be invoked to explain these latter results. The σ_I and σ_R^0 values for MR_3 substituents [14], suggest that a net electron withdrawl from the heteroaromatic π system can result from the opposition between the d_π—p_π interactions, with the d orbitals of M acting as π acceptors, and the electron donating field/inductive effects, with the former process predominating.

In contrast, when a methyl proton is replaced by a Me_3Si or Me_3Sn group, the CH_2MR_3 substituent causes a shielding of the "*ortho*"-like carbons, whereas the "*meta*"-like position was relatively unaffected. Moreover the magnitude of the former effect appeared to be related both to the nature of M, being larger for tin than for silicon derivatives, and to the substitution pattern; thus upfield shifts of 2.1 and 0.8 (XIV) and 3.3 and 1.1 ppm (XVI) were observed for the C-5 and C-3 carbons, respectively, compared with those in the parent trimethylisoxazole VII. Even larger upfield shifts (4.5 and 2.6 ppm) occur at C-4 in compounds X and IX, respectively, compared with those in VII. Interestingly, the CH_2MR_3 groups at position 3 caused lower upfield shieldings of the C-4 (0.7 and 1.2 ppm for XV and XVII, respectively, compared with the dimethyl derivative VI). All these features indicate a significant electron donation to the heterocyclic ring; it is possible to interpret the above pattern in terms of σ—π hyperconjugation. In this mechanism the polar C—M bond acts as a π electron source by both field/inductive and resonance effects according to the derived σ_I and σ_R^0 values [14] for these CH_2MR_3 substituents.

In conclusion, the silylated and stannylated isoxazoles represent perturbed heterocyclic moieties in which the ^{13}C NMR chemical shift data may provide an insight into the type and the magnitude of the electronic effects exerted by MR_3 and CH_2MR_3 substituents in the various positions of the heterocyclic ring.

Experimental

^1H and ^{13}C NMR spectra were recorded, using solutions in $CDCl_3$ with tetramethylsilane as internal standard, with Perkin Elmer R32 and Varian X-L 100 spectrometer, respectively. Mass spectra were obtained with a Varian MAT 111 instrument. Ether and THF were dried by distillation over sodium wire and $LiAlH_4$. Light petroleum refers to the fraction b.p. 30—50°C.

3,5-Dimethyl-4-(trimethylsilyl)isoxazole (II)

1.6 *M* n-Butyllithium in hexane (0.0179 mol, 11.2 ml) was added drop wise under nitrogen to a stirred, cooled (—60°C) solution of 4-iodo-3,5-dimethylisoxazole (I) [5] (4 g, 0.0179 mol) in dry ether (60 ml); during the addition the temperature was maintained between —60 and —55°C. The resulting suspension was then stirred at the same temperature for 5 h; chlorotrimethylsilane (1.94 g, 0.0179 mol) in dry ether (20 ml) was added at such a rate as to keep the temperature below —50°C. The mixture was then stirred at —55°C for 1 h, allowed to warm to room temperature, and set aside overnight. After addition of water (30 ml), the ethereal solution was separated and the aqueous phase was washed with ether (2 × 10 ml); the liquid residue after evaporation of the combined organic extracts was distilled under reduced pressure, to give compound II (2.17 g, 71.6%) as a clear, colorless oil (b.p. 45—47°C/0.1 mmHg) (Found: C, 57.0; H, 9.03; N, 8.21. $C_8H_{15}NOSi$ calc.: C, 56.8; H, 8.88; N, 8.28%); ^1H NMR: δ 0.32 (s, 9 H, $SiMe_3$) 2.26 (s, 3 H, 3-Me), 2.38 ppm (s, 3 H, 5-Me).

3,5-Dimethyl-4-(trimethyltin)isoxazole (V)

By the method reported above, the iodo derivative I (4 g, 0.0179 mol) was allowed to react with 1.6 *M* n-butyllithium (0.0179 mol, 11.2 ml) and trimethyltin chloride (3.75 g, 0.0179 mol) in dry ether (80 ml) to yield the tin isoxazole V (3.2 g, 69%) as a colorless liquid. An analytical sample was obtained by further distillation (b.p. 54—55°C/0.05 mmHg) (Found: C, 36.93; H, 5.69; N, 5.76. $C_8H_{15}NOSn$ calc.: C, 36.96; H, 5.78; N, 5.39%). ^1H NMR: δ 0.32 (s, 9 H, $SnMe_3$), 2.20 (s, 3 H, 3-Me), 2.33 ppm (s, 3 H, 5-Me).

Reaction of 4-iodo-3,5-dimethylisoxazole (I) with Mg and Me_3SiCl

As described by Kochetkov [5], compound I (8.3 g, 0.037 mol), was treated with Mg turnings (2.7 g, 0.111 mol) in dry ether (65 ml) in the presence of ethyl bromide (8.15 g, 0.074 mol); chlorotrimethylsilane (13.4 g, 0.123 mol) in the same solvent (20 ml) was then added dropwise and the mixture was stirred at room temperature for 60 h. After addition of saturated aqueous ammonium chloride (120 ml), the ethereal layer was separated, dried, and evaporated to leave an oily product (4 g), which was fractionally distilled. The fraction (1 g) boiling at 55—70°C/15—20 mm Hg consisted almost exclusively (IR and NMR) of 3,5-dimethylisoxazole (VI); further high vacuum distillation of the residue, afforded 1.7 g (27%) of the silyl derivative II, identical (IR and NMR) to the product described above. The solid recovered from the residue of the distillation was washed with a small amount of pentane and sublimed at 75°C/0.1 mmHg, to to yield tetramethyl-4,4'-diisoxazole (III) (0.9 g) (m.p. 115—116°C) (lit. [15] m.p. 114—115°C). (Found: C, 62.7; H, 6.45; N, 14.31. $C_{10}H_{12}N_2O_2$: calc.: C,

62.48; H, 6.29; N, 14.58%). ^{1}H NMR: δ 2.10 (s, 6 H, 3- and 3'-Me), and 2.25 ppm (s, 6 H, 5- and 5-Me).

General procedure for the preparation of compounds VIII, IX and X, from 3,5-dimethyl- (VI), and trimethylisoxazole (VII)

1.6 *M* n-butyllithium in hexane (0.05 mol, 31.25 ml) was added dropwise under nitrogen to a stirred, cooled solution (—70°C) of the isoxazole derivative (0.05 mol) in dry THF (80 ml), the temperature being maintained between —70 and —60°C. After 1 h at —70°C, chlorotrimethylsilane or trimethyltin chloride (0.05 mol) in the same solvent (15—20 ml) was added at such a rate as to keep the temperature below —60°C; the mixture was then stirred at —70°C for 1 h, allowed to warm to room temperature, then set aside overnight. The resulting yellow solution was evaporated and the residue was treated with light petroleum (100 ml). The solid which separated was filtered off and the filtrate evaporated to yield a liquid containing the desired silicon- or tin-isoxazole with minor amounts of the starting materials and of unidentified side products. The yields of compounds VIII, IX, and X (ca. 70, 60, and 75% respectively), were determined by GLC and ^{1}H NMR spectra, while analytical samples were obtained, as colorless liquids, by careful fractional vacuum distillation.

(a) 3-Methyl-5-(trimethylsilylmethyl)isoxazole(VIII): (b.p. 43°C/0.6 mmHg) (Found: C, 56.5; H, 8.79; N, 8.11. $C_8H_{15}NOSi$, calc.: C, 56.8; H, 8.88; N, 8.28%). ^{1}H NMR: δ 0.03 (s, 9 H, $SiMe_3$), 2.10(d, *J* 1 Hz, 2 H, CH_2), 2.16 (s, 3 H, 3-Me), and 5.56 ppm (t, *J* 1 Hz, 1 H, 4-H).

(b) 3,4-Dimethyl-5-(trimethylsilylmethyl)isoxazole(IX): (b.p. 37°C/0.03 mmHg) (Found: C, 58.90; H, 9.56; N, 7.91. $C_9H_{17}NOSi$, calc.: C, 59.02; H, 9.29; N, 7.65%). ^{1}H NMR: δ 0.04 (s, 9 H, $SiMe_3$), 1.77 (s, 3 H, 4-Me), 2.04 (s, 2 H, CH_2), and 2.12 ppm (s, 3 H, 3-Me).

(c) 3,4-Dimethyl-5-(trimethyltinmethyl)isoxazole(X): (b.p. 68—70°C/0.15 mmHg) (Found: C, 39.21; H, 6.28; N, 5.02. $C_9H_{17}NOSn$, calc.: C, 39.46; H, 6.21; N, 5.12%). ^{1}H NMR: δ 0.15 (s, 9 H, $SnMe_3$), 1.80 (br, s, 3 H, 4-Me), 2.14 (s, 3 H, 3-Me), and 2.22 ppm (br, s, 2 H, CH_2).

Reaction of 3,5-dimethyl-4-(chloromethyl)isoxazole(XI), with Mg and Me_3SiCl in ether

The chloromethyl derivative XI [16] (4.65 g, 0.032 mol) in dry ether (20 ml) and methyl iodide (3 g, 0.021 mol) in the same solvent (20 ml) were added simultaneously dropwise with vigorous stirring to Mg turnings (1.29 g, 0.053 mol) under a layer of ether (10 ml), and the mixture was stirred at room temperature until the metal was almost completely consumed. Chlorotrimethylsilane (7.3 g, 0.067 mol) in dry ether (20 ml) was then added and the mixture was refluxed for 2 h. After addition of saturated aqueous ammonium chloride (50 ml), the ethereal layer was separated, dried, and evaporated to dryness; the solid residue was treated with light petroleum (30 ml), filtered, and sublimed at 90°C/0.3 mmHg to give 1,2-bis(3,5-dimethylisoxazol-4-yl)ethane (XIII) (2.3 g, 65%) m.p. 133—134°C (Found: C, 65.55; H, 7.36; N, 12.35. $C_{12}H_{16}N_2O_2$ calcd.: C, 65.43; H, 7.32; N, 12.72%). ^{1}H NMR: δ 2.01 (s, 6 H, 2 × 3-Me), 2.05 (s, 6 H, 2 × 5-Me), 2.40 ppm (s, 4 H, 2 × CH_2). GLC-MS analysis of the filtrate revealed the presence of compound XIII as main component, with lesser amounts of 3,5-

dimethyl-4-(trimethylsilylmethyl)isoxazole (XIV) and other unidentified products.

3,5-Dimethyl-4-(trimethylsilylmethyl)isoxazole (XIV)

Chlorotrimethylsilane (11.3 g, 0.104 mol) and Mg turnings (1 g, 0.041 mol), previously activated by heating with a crystal of iodine at 60—70°C under nitrogen, were refluxed for 30 min in dry THF (15 ml). 3,5-Dimethyl-4-(chloromethyl)isoxazole (XI) (5 g, 0.034 mol) in the same solvent (5 ml) was added dropwise very slowly (ca. 2 h) and the mixture was then refluxed under nitrogen for a further 2 h. After removal of the solvent, the residue was treated with light petroleum (50 ml) and filtered; evaporation of the filtrate left an oily product which was distilled at 72—74°C/3 mmHg to give the isoxazole derivative XIV (3.8 g, 60%). An analytical sample was obtained by further distillation (b.p. 69—71°C/1 mmHg) (Found: C, 58.75; H, 8.98; N, 7.62. $C_9H_{17}NOSi$, calcd.: C, 59.02; H, 9.29; N, 7.65%). ^{1}H NMR: δ 0.15 (s, 9 H, $SiMe_3$), 1.72 (s, 2 H, CH_2), 2.24 (s, 3 H, 3-Me), 2.33 ppm (s, 3 H, 5-Me).

5-Methyl-3-(trimethylsilylmethyl)isoxazole(XV)

By the method described above, 5-methyl-3-(chloromethyl)isoxazole(XII) [7] (2.3 g, 0.0175 mol) was treated with Mg (0.45 g, 0.0185 mol) and Me_3SiCl (5.5 g, 0.051 mol) in dry THF (10 ml) to give the silylated isoxazole (XV) (1.45 g, 49%) (b.p. 32—34°C/0.04 mmHg) (Found: C, 56.35; H, 8.68; N, 8.35 $C_8H_{15}NOSi$, calcd.: C, 56.70; H, 8.86; N, 8.27%). ^{1}H NMR: δ 0.07 (s, 9 H, $SiMe_3$), 2.02 (s, 2 H, CH_2), 2.33 (d, *J* 1 Hz, 3 H, 5-Me), 5.68 ppm (q, *J* 1 Hz, 1 H, 4-H).

3,5-Dimethyl-4-(trimethyltinmethyl)isoxazole(XVI)

Trimethyltinlithium (5.12 g, 0.03 mol) in dry THF (30 ml), freshly prepared by the method of Tamborski [17], was added dropwise under nitrogen with vigorous stirring to a cold (—60°C) solution of the chloromethyl derivative XI (3 g, 0.021 mol) in the same solvent (15 ml). The mixture was then stirred at —50°C for 4 h, allowed to rise slowly to room temperature, and set aside overnight. After removal of the solvent, the semi-solid residue was treated with light petroleum (30 ml) and filtered to remove the inorganic material. Evaporation of the filtrate left an oil, which was purified by fractional vacuum distillation to yield compound XVI (2.25 g, 40%) (b.p. 94—95°C/0.3 mmHg) (Found: C, 39.70; H, 6.4; N, 4.93. $C_{19}H_{17}NOSn$, calcd.: C, 39.46; H, 6.21; N, 5.11%). ^{1}H NMR: δ 0.12 (s, 9 H, $SnMe_3$) 1.82 (s, 2 H, CH_2), 2.15 (s, 3 H, 3-Me), 2.26 (s, 3 H, 5-Me).

5-Methyl-3-(trimethyltinmethyl)isoxazole (XVII)

Similarly, 5-methyl-3-(chloromethyl)isoxazole (XII) (2.4 g, 0.0182 mol) was treated with trimethyltinlithium (4.65 g, 0.0273 mol) in dry THF (40 ml) to give compound XVII (2.13 g, 45%) as a colorless oil (b.p. 89—90°C/3—4 mm Hg) (Found: C, 37.30; H, 5.60; N, 5.58. $C_8H_{15}NOSn$, calcd.: C, 36.97; H, 5.78; N, 5.39%). ^{1}H NMR: δ 0.12 (s, 9 H, $SnMe_3$), 2.13 (s, 2 H, CH_2), 2.32 (d, *J* 1 Hz, 3 H, 5-Me), 5.62 ppm (q, *J* 1 Hz, 1 H, 4-H).

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